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PB80-139918

Assessment of Vertical Distributions of Photochemical Pollutants and Meteorological Variables in the Vicinity of Urban Areas

SRI International, Menlo Park, CA

Prepared for

Environmental Protection Agency, Research Triangle Park, NC

Aug 79

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-79-017
August 1979

PB80-139918

Air

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/4-79-017

2.

3. RECIPIENT'S ACCESSION NO.
PB 80 139918

4. TITLE AND SUBTITLE
Assessment of Vertical Distributions of Photochemical Pollutants and Meteorological Variables in the Vicinity of Urban Areas

5. REPORT DATE
August 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
F.L. Ludwig

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

10. PROGRAM ELEMENT NO.
2AA635

11. CONTRACT/GRANT NO.
68-02-2662

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Air, Noise and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A system for classifying vertical profiles of ozone and other photochemical pollutants has been derived by analyzing 268 ozone profiles obtained from published reports and EPA data files — 93 from St. Louis, 40 from Los Angeles, 30 from Houston, 31 from Washington, D.C., 53 from Toronto, and the remaining 21 from Indianapolis, Tampa, and Denver. The profiles fall into six different categories that are related to the relative importance of the following factors: destruction of zone near the surface, vertical mixing, and photochemical production. Vertical mixing tends to produce profiles that are nearly uniform with height. Strong mixing offsets the destruction at the surface. Unless effective vertical mixing of ozone occurs, destruction at the surface will produce profiles with steeply increasing concentrations with height in the lowest layers. The report presents and discusses 108 representative examples of the vertical profiles, most with corresponding temperature data and many with aerosol (nephelometer), NO_x, or hydrocarbon data. Linear regression has been used to define the relation between ozone concentrations in the mixing layer and those aloft, for the different profile types. The locations relative to an urban area and the times when each profile type is most apt to occur are discussed in terms of the statistics of the data set and the physical processes involved.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone	Temperature Profiles		
Oxidants	Temperature Inversions		
Photochemical	Hydrocarbons		
Nitrogen dioxide	Aerosols		
Nitrogen oxide	Nephelometer		
Meteorological	Mixing height		
Vertical Profiles			

18. DISTRIBUTION STATEMENT

19. SECURITY CLASS *(This Report)*

20. SECURITY CLASS *(This page)*

21. NO. OF PAGES
185

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/4-79-017

ASSESSMENT OF VERTICAL DISTRIBUTIONS
OF
PHOTOCHEMICAL POLLUTANTS AND METEOROLOGICAL VARIABLES
IN THE VICINITY OF URBAN AREAS

by

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SRI Project 6869

Contract No. 68-02-2662

Project Officer
E.L. Martinez

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR, NOISE AND RADIATION
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

August 1979

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Publication No. EPA-450/4-79-017

ACKNOWLEDGMENTS

Numerous people helped in the preparation of this report. Kenneth Nitz, Eugene Shelar, Rosemary Maughan, Frances Adams, and Kathleen Chaiken assisted with data processing and analysis. Joyce Kealoha, L.H. Wu, Jack Byrne, Shirley Bartels, Jane Hazlett, and Josette Louvigny assisted in the preparation of the figures and text.

E. L. Martinez and Warren Freas of EPA had many valuable suggestions during the course of the research. Messrs. Martinez and Freas, along with Dave Mage of EPA, provided most of the data necessary for the analyses described in this report. Mr. Dale Coventry of EPA also provided data and was extremely helpful with calculations of air trajectories.

ABSTRACT

A system for classifying vertical profiles of ozone and other photochemical pollutants has been derived by analyzing 268 ozone profiles obtained from published reports and EPA data files--93 from St. Louis, 40 from Los Angeles, 30 from Houston, 31 from Washington, D.C., 53 from Toronto, and the remaining 21 from Indianapolis, Tampa, and Denver. The profiles fall into six different categories that are related to the relative importance of the following factors: destruction of ozone near the surface, vertical mixing, and photochemical production. Vertical mixing tends to produce profiles that are nearly uniform with height. Strong mixing offsets the destruction at the surface. Unless effective vertical mixing of ozone occurs, destruction at the surface will produce profiles with steeply increasing concentrations with height in the lowest layers. The report presents and discusses 108 representative examples of the vertical profiles, most with corresponding temperature data and many with aerosol (nephelometer), NO_x, or hydrocarbon data. Linear regression has been used to define the relation between ozone concentrations in the mixing layer and those aloft, for the different profile types. The locations relative to an urban area and the times when each profile type is most apt to occur are discussed in terms of the statistics of the data set and the physical processes involved.

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SUMMARY AND CONCLUSIONS

A. Findings

1. General

The development of effective ozone control strategies requires at least some basic knowledge of the three-dimensional distribution of photochemical pollutant concentrations and meteorological conditions. Available information, however, is usually limited to a few observations made near the surface. The objective of this study has been to develop a characterization of the three-dimensional nature of the atmosphere which might be inferred from the surface observations and perhaps, a few measurements obtained aloft. Those special studies where vertical profiles of pollutant concentrations were measured around cities have served as the starting point for the study.

The open literature and the U.S. Environmental Protection Agency (EPA) have provided 268 vertical profiles of ozone from seven different areas that have been studied in detail and classified. The data base included 93 profiles from the St. Louis area, 40 from the Los Angeles Basin, 30 from the Houston area, 31 from the Washington, D.C. area, and smaller numbers from Toronto, Indianapolis, and Tampa. Most of the profiles are accompanied by measurements of the vertical distribution of temperature; in many cases, the vertical distribution of one or more of the following parameters is also available: dew point, aerosol backscatter (Bscat), oxides of nitrogen (NO_x), total hydrocarbons (THC), and nonmethane hydrocarbons (NMHC).

Careful examination of the pollutant profiles in general, and the ozone profiles in particular, showed that their shapes could be classified into six categories, shown in the figure on the next page (Figure 4 in the text). The shapes are determined by three different physical processes: vertical mixing, surface generation or destruction, and photochemical production. Section III presents many of the vertical profiles from the cities of St. Louis, Los Angeles, Houston, and Washington and discusses the classification of the profiles.

2. Types of Pollutant Profiles

a. Type A Profile

The Type A profile is characterized by nearly uniform concentrations with height. Such profiles are produced when the vertical mixing is strong enough to offset destruction of the ozone at the surface and when little or no ozone is being formed from precursors within the boundary layer. Thus, one might expect this to be the most common profile during the forenoon, when mixing is likely to be reasonably good but the photochemical production of ozone is not as pronounced as during the afternoon. The data confirm the expectations: about 45 percent of all profiles measured between 0900 and 1200 Local Standard Time (LST) were of Type A. About 55 percent of the measurements during this morning time period upwind or to one side of the city fell in this category if only profiles measured upwind or to one side of the city were considered.

b. Type B Profile

The Type B profile is similar to the Type A except that concentrations in the lowest layers are much less than they are at higher altitudes, because destruction processes near the surface dominate vertical mixing. Ozone is destroyed much more rapidly near the surface than it can be replaced by mixing from aloft. This situation can arise when the mixing is inhibited by a stable layer at the surface or when the destruction processes are very strong because of the presence of considerable amounts of nitric oxide (NO). Nitric oxide will be present near the surface in areas of strong emissions. A stable layer will frequently form at the surface with nighttime cooling of the ground or when air passes over a colder surface, such as a body of water in the summertime. Few Type B profiles were observed, but this was probably because there were very few measurements available from nighttime hours. None of the 13 profiles categorized as Type B were measured after 1030 LST during the daytime. Nine of the 13 were measured between 2100 and 0900. One might expect that with the onset of mixing during the morning, Type B profiles would evolve into Type A profiles.

c. Type C Profile

A Type C profile is characterized by concentrations that are greatest near the ground and tend to decrease with height to the top of the mixing layer, remaining relatively constant above it. We believe this type of profile is most likely to occur during periods when photochemistry is proceeding rapidly and vertical mixing is strong enough to offset surface destruction processes, but has not proceeded to the point where ozone formed from precursors near ground level has been mixed throughout the boundary layer. One would expect a Type C profile to be most common in the afternoon and, as it turned out, more than three-fourths of the 21 times C profiles were observed were between noon and 1800 LST. None was observed at night.

d. Type D Profile

With continued mixing, a profile of Type C should evolve into a Type D profile. Type D displays nearly uniform concentrations throughout the mixing layer and a rapid decrease with altitude at the mixing layer's top. The processes leading to a Type D profile are the same as those leading to a Type C profile, but the mixing is more complete. It is sometimes difficult to distinguish between these two types of profiles. Type D profiles were second most common among the profiles examined in this program; 68 of the 268 classified cases were of this type. As with the Type C profiles, they were most frequent during the afternoon hours; nearly 80 percent occurred between noon and 1800 LST.

e. Type E Profile

The Type E profile bears much the same relationship to a Type D profile as Type B does to Type A. Above the lowest layers, Type E and D profiles are similar. The surface concentrations are much less with a Type E, because these profiles are formed when destructive processes at the surface more than offset vertical mixing that brings ozone down from aloft. A Type E profile will form either when vertical mixing is inhibited by the formation of a stable layer at the surface, or when surface destruction processes are particularly pronounced. As with Type B, Type E profiles are not common during the afternoon; about two-thirds of the 32 profiles classified as Type E were measured before noon. However, this may be somewhat misleading because very few measurements were made at night. If more measurements were available, one might expect to find many Type E profiles during the early evening when the ozone formed by afternoon photochemical processes would be destroyed in the stable layer forming at the surface. The elevated layer formed in this way is likely to be found farther downwind in suburban and rural areas later at night and during the early morning hours.

f. Type F Profile

If a Type E profile persists through the night, it may evolve into a Type F profile during the following morning. As the mixing layer develops and becomes deeper during the morning, the ozone trapped in the layer aloft during the night will be eroded and mixed downward into the mixing layer. If the mixing never reaches the height that it did on the preceding day, then the Type F profile will last through the afternoon. However, this should be less common and one would expect to find Type F profiles most frequently during the morning hours. Of the 54 cases classified as Type F, nearly 80 percent were found between 0600 and noon LST.

3. Mixing Depth Changes During the Day

It is obvious from the preceding section that the type of profile present and the transitions from one type of profile to another depend heavily on changes in atmospheric stability and the depth of the mixing layer. It is therefore important to know something of the typical diurnal cycle of the mixing depths, especially for the clear, warm, light-wind conditions that usually accompany high ozone concentrations (Meyer et al., 1976; Ludwig et al., 1977).

On clear nights outside the city, a stable layer is likely to develop at the surface and extend upward for a few hundred meters. Within the city, the formation of this surface-based stable layer is inhibited by the heat released by power consumption, air conditioning, space heating, and the heat stored by the thermal mass of all the city's buildings. There is some empirical evidence suggesting a minimum mixing depth over a city. This minimum mixing depth is dependent on city size, but in general, it will be of the order of 100 meters or so (Ludwig and Dabberdt, 1973).

During the afternoon, the heating of the lower layers of the atmosphere will cause mixing to reach its greatest heights. In general, these heights will be from a few hundred to a few thousand meters; they can usually be estimated from temperature profiles available from radiosonde stations in the morning and afternoon. Usually the mixing depth during the afternoon will be lower on days with high ozone concentrations. The transitions between daytime and nighttime mixing depths take place rapidly, especially the evening transition. Around sunset, a stable layer forms very rapidly near the surface outside the city. The corresponding transitions to Type B or Type E ozone profiles (from Type A or Type D) will probably occur somewhat later, because destruction of the ozone already within the stable layer takes time.

The morning transition from nighttime to daytime mixing conditions takes place more slowly, because it takes a finite period of time for the heating to overcome the effects of the night's cooling of surface layers. The data suggest that this transition can take anywhere from 1 or 2 hours to 5 or 6 hours. If there is a strong subsidence inversion above the surface but at a relatively low altitude, surface heating will cause the mixing to reach the altitude of that inversion fairly quickly, and then it will rise only slowly thereafter. Subsidence inversions are frequently a feature of high-pressure areas, which are known to be favored areas for the development of high ozone concentrations when sufficient precursor sources exist.

The preceding discussion applies primarily to simple continental geographic locations, but in more complicated locations, such as those near land-water interfaces, the mixing layer may behave in a more complicated fashion. For instance, if air moves from a warmed land surface to a colder water surface, the effect will be similar to that which occurs at night. The air will be cooled from below and a stable layer will form near the surface. Within this stable layer, the ozone may be destroyed and there will be a transition from a Type D to a Type E profile or from a Type A to a Type B profile, even in the daytime, when one might not expect such transitions to occur. Sometimes synoptic meteorological conditions will cause convective mixing at night that will produce a transition from a Type B to a Type A profile, even though this transition is much more frequently associated with the onset of daytime heating.

4. Evolution of Profile Types

This section discusses the typical evolution of profiles during the day as air moves over an urban area. It should be remembered that there are other, atypical ways in which the same or different transitions might occur. Imagine a column of air upwind of a city during the early morning hours. This column of air has traveled for a considerable period of time without having been exposed to major sources of pollution. Ozone concentrations are near "background" values (a few tens of ppb) and distributed uniformly with height, except near the surface. Because it has been a clear night, a shallow stable layer has formed near the surface, and much of the ozone within that layer has been destroyed by contact with the surface. Thus the vertical distribution of ozone within our column is Type B. As the column moves toward the city and the sun rises, the ground begins to heat. As the heating continues, the stable layer is gradually destroyed and the ozone aloft is mixed down, so that the vertical distribution of ozone becomes nearly uniform with height, a Type A profile.

As the air enters the city, perhaps around 0900 LST, it encounters the NO emissions from the city, and considerable ozone in the lower layers is destroyed. Mixing above the city may not be sufficiently vigorous to replace the destroyed ozone, so the profile can revert to Type B. As the column of air leaves the city, the photochemical processes act on the hydrocarbons and oxides of nitrogen that have been introduced into the lower layers of the atmosphere, and ozone is produced. The mixing of precursors and ozone has not gone on long enough to distribute ozone throughout the mixing layer, so a Type C profile results.

As the column of air travels farther downwind of the city, mixing continues, and soon the ozone and precursors are distributed uniformly within the mixing layer. Thus, the Type C profile evolves into a Type D profile. By now it is late afternoon or early evening and the surface has begun to cool. A stable layer forms near the surface and much of the ozone within that stable layer is destroyed, leading to the Type E profile (see, e.g., Harrison et al., 1978). It was noted earlier that the Type E profile could also be formed if the column of air passed over a cold surface, such as a body of water.

The Type E profile formed in our column of air will probably persist through the night, unless weather patterns develop that cause the atmosphere to be unstable and nighttime mixing to occur. If this should happen, the profile might evolve back into a Type D profile, and the concentrations at the surface would increase anomalously at night. Ludwig and Shelar (1978) have observed some nighttime instances of high ozone concentrations when this anomalous transition from Type E to Type D seems to have occurred. A more usual situation is for the Type E profile to evolve into a Type F during the next day's morning heating period (see, e.g., Johnson and Singh, 1977). If the heating and mixing proceed to the point where the mixing depth is equal to, or greater than, what it was on the preceding day, the profile will change back to a Type D once again. As time goes on and more and more ozone is lost, the Type D profile will revert to a Type A profile unless more pollutants are introduced and more ozone is formed photochemically.

If, as will be the case under the worst of conditions, the air remains in a region of emissions or passes successively over one emissions area after another, the concentrations within the mixing layer will continue to build up. The Type D profiles will become more and more pronounced and the concentrations within the mixed layer will become greater and greater, while those aloft will change very little.

B. Applications of Findings

1. General

There have been two goals for the research summarized here. The first was to use the existing data to describe and improve our understanding of the processes that affect the vertical distribution of photochemical pollutants, particularly ozone, in the atmosphere. The second goal was to take that general description and use it as a basis for analyzing specific cases. That is, some quidelines are sought by which conventional surface pollutant measurements and routinely available meteorological observations might be used to infer the concentrations aloft, especially during periods when the national ambient air quality standards (NAAQS) were violated.

Knowing the distribution of ozone around a city is fundamental to developing strategies for reducing pollution. Even the simplest modeling approaches--e.g., the empirical kinetic modeling approach (EKMA)--require knowledge of the concentrations in the mixing layer entering the city and those in the mixing layer downwind of the city (Office of Air Quality Planning and Standards, 1977, 1978). Certain relationships are assumed between precursor emissions within the city and the concentrations within the mixing layer downwind. One can then postulate changes in emissions and use the EKMA or some other model to estimate how the downwind ozone concentrations would be changed. More complicated models require similar kinds of information, but in greater detail. The following sections provide some guidelines on how the results of this research might be applied to specific situations.

2. Assessment of Air Quality Conditions from Limited Surface Data

a. Background" Conditions

The data have shown that when a Type A or D profile is present, surface measurements of ozone will do a good job of characterizing mixing-layer concentrations. The data also indicate that the Type A or D profiles can reasonably be expected to accompany well-established vertical mixing. The question then becomes one of determining when mixing has proceeded far enough to have established a relatively uniform vertical pollutant profile. Several routinely measured parameters are available that can be used as guides. One of these is the ozone concentration itself. During the morning, one might expect to find a relatively rapid rise in ozone concentration accompanying the onset of mixing; this rapid rise in the morning would be uncharacteristic of photochemical production because of the hour of the day. Temperature might also rise rather rapidly during the early morning because the effects of solar heating would be confined to the shallow layer within the surface-based nocturnal inversion, at least until that inversion was erased by the heating. Finally, wind speed can be used as a guide to determining when mixing has taken place in the morning. Momentum is continually being transferred downward to replace that lost at the surface by friction. When this vertical transfer is inhibited, there are likely to be near-calm winds, but when the mixing is reestablished the wind speed should rise rather pronouncedly.

Routine data can be used to determine when measurements at surface locations outside the city are representative of concentrations through the mixing layer. If the location is upwind of the city, these measurements will certainly be representative of the "background" conditions. Even if the available measurements are downwind, they might still be useful for estimating the "background" conditions if vertical mixing occurs sufficiently early in the day that little photochemical activity would have taken place, say before about 1000 LST.

The data have shown that after about noon, it can usually be safely assumed that good vertical mixing has taken place. However, it cannot always be assumed that the concentrations entering the city during the afternoon are representative of the "background" conditions that prevailed early in the day. Some of the data from this study suggest that new photochemical ozone might form in "background" air, even when no new precursors have been added. Presumably, this new ozone forms from residual precursors.

b. Concentrations Above and Downwind of the City

It is very important that any ozone-monitoring site within a city be well removed from local sources of NO, but this does not seem to be sufficient to ensure that the data from such a station can be used to describe conditions throughout the mixing layer above the city. In general, the stations of the Regional Air Pollution Study (RAPS) are well located, but nevertheless give readings that were substantially less than the concentrations in the mixing layer, even in cases where Type A profiles were well established in the areas outside the city. However, the St. Louis data do show that ozone concentrations above the surface effects were fairly uniform throughout the region during the morning hours. Thus, measurements made outside the city can be used to estimate concentrations over the city--above the destructive effects of NO emissions. During the afternoon, in lieu of better information, one might assume that the upwind conditions prevailed to about the center of the city; interpolation could then be used to estimate conditions from the center of the city to a downwind point where data are available.

The interpolation between the center of the city and a downwind location could be aided by the use of a simple Gaussian model. For example, Turner's (1970) workbook shows how the depth to which emissions will mix will increase with travel distance, for different classes of atmospheric stability. The atmospheric stability classes can be determined from conventional meteorological measurements (Turner, 1964; Ludwig and Dabberdt, 1976). These considerations could be used to estimate the transition of the vertical profile from the Type C to the Type D case.

3. Modeling

It is apparent from the discussion in the preceding section that the distribution of ozone around a city can be estimated reasonably well, if sufficient surface pollutant and meteorological data are available. Complex models require estimates of morning conditions throughout the area as inputs. The model's outputs describe the three-dimensional ozone distribution for later in the day. These outputs must be compared with the estimates obtained from the available surface-ozone observations. It might well be that good mesoscale meteorological models could be used to provide better estimates of the mixing and transport, and to improve the estimates of pollutant distribution around the city. Obviously, it would be better if comprehensive airborne measurements were available as inputs for the model and the required validation data, but this would be prohibitively expensive for most routine applications. Certainly, special programs such as the RAPS are warranted for model development and validation, but it appears that reasonable estimates of the necessary inputs can be obtained from more routine measurement programs, especially if the ozone monitoring sites are placed away from local influences in areas where their data can be used to characterize conditions through the mixed layer.

4. Selection of Monitoring Sites

The analysis of the data makes it clear that ozone monitoring sites within a heavily populated area are not apt to be as useful as those outside the area. It is not the purpose of this research to develop comprehensive guidelines for siting monitoring stations, but it is worth pointing out that three or four locations outside a city would provide very valuable information for most practical applications. The locations of those sites relative to the city would depend on wind directions and numerous other considerations (see, for example, Ludwig and Shelar, 1978). Sites outside the cities would provide estimates of the incoming "background" conditions and the ozone formed from the precursors emitted within the cities. The precursor concentrations should probably be characterized by measurements within the urban area.

C. Remaining Shortcomings

As is always the case, the data base has some shortcomings, and the analysis could not include everything that one might hope for. However, the data base is much more comprehensive than was expected when the work began, its most important shortcoming being the relative absence of nighttime cases. With more nighttime cases available, the characteristics of Type B and E profiles could be better defined.

Some kinds of data that are available were not analyzed during this project. For example, vertical profiles of ozone in rural areas were not studied, although at least some data are available from such areas. The study was also limited to the lower parts of the atmosphere, leaving out studies of stratospheric intrusions or other interchanges with the stratosphere. Perhaps, at some future date, it would be worthwhile to develop a more comprehensive characterization of the three-dimensional distribution of ozone by including data from higher altitudes and from less urban areas.

Finally, time, money, and contractual limitations have kept us from exploring the possibility of using the temporal histories of pollutant concentration and meteorological variables to determine objectively the likely vertical profiles for an area. At present, the general subjective guidelines given earlier are available, but it might be worthwhile to examine the data more carefully in the future to see if objective techniques can be devised. Even without such objective techniques, the analyses presented here provide the information required for estimating conditions aloft from surface observations.

I INTRODUCTION

A. Purposes of the Study

The meteorological and chemical processes involved in the production of atmospheric oxidants are all three-dimensional; consequently, the development of effective control strategies for ozone requires an understanding of the three-dimensional distributions of photochemical pollutants--principally oxides of nitrogen, nonmethane hydrocarbon, and, most important, ozone. Meteorological conditions play an important role in the production, destruction, and transport of photochemical pollutants. Therefore, it is also important to know something of the three-dimensional behavior of the atmosphere itself. Most routine measurements of air pollution are confined to the surface, leaving a void in our knowledge of the vertical distributions. The purpose of the research described in this report has been to fill that void by making use of the considerable amount of three-dimensional data (from aircraft and sounding devices) that have been collected in recent years.

The analyses of the data have been directed toward finding ways of estimating vertical distributions of the photochemical pollutants in the vicinity of urban centers, when no special measurements have been made at higher altitudes. Toward this end, we have sought to characterize the vertical profiles and relate them to more commonly available kinds of information, such as time of day, conventional meteorological observations, and location relative to the city itself. Ultimately, the results are intended to be useful for formulating oxidant control strategies; they will provide the basis for estimating the effects of the uncontrollable levels of oxidant and its precursors that are apt to enter a city from the upwind direction, and also for estimating total impacts by considering ozone concentrations at higher altitudes that can be injected into the mixing layer when that layer deepens. Thus we are not limited to consideration only of what is observed at the surface.

B. Sources of Data

1. Background

No measurements were made as part of this project. All the analyses that follow are based exclusively on data that were collected either routinely or during the course of special projects. The work began with a survey to find data that might be appropriate to the purposes of this project. It was originally planned that five cities be selected for intensive study. However, during the course of the project, it was decided that the extensive study of four cities and somewhat less detailed analysis of data from other data sources would be preferable. The following cities were considered: St. Louis, Missouri; Houston, Texas; Washington, D.C.; Los Angeles, California; Toronto, Canada; Indianapolis, Indiana; the urbanized area of New York, New Jersey, and southern New England; Tampa, Florida; Dayton/Columbus, Ohio; the San Francisco Bay Area; Fresno and Bakersfield, California; and Tulsa, Oklahoma.

The first four cities on the list were chosen for detailed analysis. Although the choice of the cities was subjective, it was based on fairly well-defined criteria. The criteria were

- Quality of the data; we have tried to avoid unreliable data that could be misleading.
- Quantity of the data; in choosing among areas that were generally equal in most other respects, we opted for the area with the larger data set.
- Form of the data; data in computer-compatible, or already displayed graphically, were judged to be more desirable because analysis was easier and less time had to be spent on tedious data-reduction processes.
- The magnitude of photochemical air-quality problems; this was judged to be an important factor because of the practical considerations underlying the project.
- Geographical diversity; this was sought because the potential for practical application of the results dictated that a wide variety of climatological and geographical conditions be studied, so that the results would be as general as possible.
- Availability of data; some data sets were not considered because they had been collected for proprietary reasons; other data sets were not available in time for use.

The areas selected for study and the reasons for their selection are discussed in the next section. The amounts and kinds of data that were available for analysis will be discussed in more detail later.

2. Primary Areas Selected for Study

a. St. Louis

The Regional Air Pollution Study (RAPS) in St. Louis provided one of the most comprehensive collections of air-quality data available anywhere. Furthermore, all the hourly surface data from 24 stations in the St. Louis area were completely reduced and available on magnetic tape for the year 1976. In many cases, these same stations also provided meteorological information such as wind speed and direction, temperature, humidity, and so forth. Furthermore, special radiosonde and pilot balloon measurements were available from four locations in the St. Louis area for the months of July and August 1976. Laser radar (lidar) and acoustic sounder records were also on hand to characterize the behavicr of the mixing layer for part of the period. Concentrations of ozone in the area are known to exceed the National Ambient Air Quality Standards

(NAAQS), which further supports the choice of St. Louis as a study area. Finally, St. Louis is representative of midwestern cities and certainly there are more data available from St. Louis than from any other midwestern location.

b. Los Angeles

Los Angeles is the classic city for photochemical pollution and probably deserves to be included in any list of cities to be studied for that reason, if for no other. Its warm climate, its subsidence inversions, and the California-type emissions all require consideration, if the study is to be general. In 1973, the Coordinating Research Council sponsored an extensive program of helicopter measurements of air quality in the Los Angeles Basin. Several other agencies, including the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB), also participated in the Los Angeles Reactive Pollutant Program (LARPP). The computer-compatible data from this program (Parker and Martinez, 1975) were available and Johnson and Singh (1977) had identified and plotted most of the usable vertical profiles from this data set, further increasing its usefulness. Other data collected by Blumenthal et al. (1974) were also available.

c. Houston

Houston has some unique characteristics that make it a candidate for study. It has a particularly high density of petrochemical industries with concomitant hydrocarbon emissions. It lies along the Gulf coast, with warm, humid summers. Photochemical air pollution is known to be a problem in the Houston area, so the area has the geographical location and the air quality problems that make it worth including in the list of cities to be studied.

In recent years, at least two fairly extensive aircraft measurement programs have been undertaken in the Houston area. One of these (Shauck and Alexander, 1978) was sponsored by the Houston Chamber of Commerce as part of their Houston Area Oxidant Study (HAOS). Another extensive aircraft monitoring project was conducted by Washington State University (Westberg et al., 1977) under the sponsorship of the EPA. The data from the EPA-sponsored study has proven to be more useful for two reasons. While computer-compatible data were not available from either study, graphical representations of the vertical ozone and temperature profiles were available from the report of Westberg et al. (1977). Furthermore, the vertical profiles from the Westberg study generally seemed to provide more information about upwind and downwind conditions than did the HAOS study. Also, the vertical profiles generally began nearer the ground and had better vertical resolution in the Westberg data set than in the HAOS data. The HAOS project had assembled most of the relevant surface meteorological and air-quality data (see Ludwig et al., 1978) necessary to supplement the Westberg data, and they were in computer-compatible form.

d. Washington, D.C.

Once the West Coast, Midwest, and Gulf Coast areas were represented, the one remaining area with major photochemical air-quality problems was the east coast. Certainly the coastal corridor from Philadelphia to Boston is a logical place to study, especially in view of the fact that many aircraft measurements are available from the area (e.g., Spicer, et al., 1976; Siple et al., 1976; Washington State University, 1976; Wolff et al., 1975) and are in computer-compatible form (Ruff et al., 1977). However, these data had already been extensively analyzed, especially by Ludwig and Shelar (1977), so we decided to direct our efforts to a different area, while still making use of the analyses already available from southern New England.

The only other east coast area for which aircraft data are known to be available is the region surrounding Washington, D.C. and Baltimore, Maryland. Good aircraft data, in computer-compatible form, were collected by the EPA (Fitzsimmons, et al., 1978) during the latter half of August, 1976. Although the surface air quality and meteorological measurements were not as extensive as could be desired, we nevertheless chose Washington, D.C. because the analysis of the available data would add another city with somewhat different characteristics to the existing inventory of information.

e. Other Areas

As noted earlier, we decided to supplement detailed analyses of data from the four cities named above with studies conducted in other areas. In this regard, the aforementioned analyses of New England data by Ludwig and Shelar (1977) have proven to be quite useful, as have those of Lovelace, et al. (1975) from the Indianapolis area and the work of Wiebe et al. (1975) in the Toronto area. Some obvious gaps remain in the geograhical coverage, particularly the Pacific Northwest and the Rocky Mountain areas. Photochemical pollution problems in the Northwest are not generally as severe as in other parts of the country. However, the mountain states and areas such as Denver should be considered for more intensive analysis as more data become available.

C. General Approach

After the major data sources had been identified and the cities selected for intensive study, we acquired the necessary data and prepared them for analysis. In general, this report is devoted to the results of the analysis from that point on. The conduct of the analysis can be divided into four parts, as follows:

- The classification of the observed vertical profiles of the photochemical pollutants, especially ozone, according to the shape of those profiles.
- The consideration of those factors that govern the distribution of ozone and other photochemical pollutants in the atmosphere.
- The determination of how the different types of vertical air pollutant profiles relate to those factors that govern the distribution of ozone and other photochemical pollutants in the atmosphere.
- The development of rules and methods for determining just what kind of vertical profile might be expected, based on conventional meteorological and surface-based air-quality information.

This report is organized along the lines just described. The next section presents a discussion of those factors that govern the vertical distribution of pollutants in the vicinity of urban areas, the kinds of vertical profiles that have been observed, and how they are related to those factors. Although the discussion proceeds from the physical processes to the profile shapes that result from those processes, the actual research took a somewhat different course. The major categories of profile shape were recognized from the available data and from a knowledge of the processes. The classification system that is described here evolved from the simultaneous consideration of theory and observation. The third section of the report presents examples from the cities selected for intensive study and from other areas, to illustrate the different types of profiles and when they tend to occur in relationship to the cities, times of day, and meteorological conditions. The report includes a summary of the findings and a discussion of how those findings can be applied to the real problem of estimating the three-dimensional distribution of ozone and the other photochemical pollutants in the vicinity of cities, when only surface measurements and conventional meteorological data are available.

II PHYSICAL PROCESSES GOVERNING PHOTOCHEMICAL POLLUTANT DISTRIBUTIONS IN THE VERTICAL AND CONSEQUENT PROFILES

A. Factors Governing the Vertical Distributions of Ozone in the Vicinity of Urban Areas

1. Background

The processes governing the distribution of ozone in the atmosphere are reasonably well understood qualitatively, if not quantitatively. The sources of ozone in regions well removed from urban areas are subject to some controversy, especially with regard to their relative magnitude. However, regardless of the source, it seems reasonably well established (e.g., Singh et al., 1978) that the yearly mean concentration of background ozone in the troposphere at midlatitude is a few tens of parts per billion.

It is worth examining how this natural ozone behaves, because it provides a convenient introduction into the processes governing the vertical distribution of ozone in the atmosphere. It is also quite easy to mistake the natural ozone behavior for similar behavior observed for ozone of anthropogenic origin. Singh, et al., (1977) have provided an idealized depiction of the behavior of natural ozone in remote locations. Figure 1 is a schematic representation based on a figure from their report. It shows that there is a large reservoir of ozone aloft and that this reservoir is relatively unaffected by daily short-term changes. The diurnal variation in ozone concentration above the mixed layer is rather small, but, as shown on the right-hand side of the figure, there can be considerable variability in the concentration at the surface during the day. This diurnal variation at the surface results from the ozone that is within or below the nocturnal inversion being destroyed and not replaced by ozone from aloft; the presence of the nocturnal inversion inhibits mixing. However, after the sun rises and the ground is warmed, there will be convective mixing, which will bring ozone from the reservoir aloft down to ground level, to replace that which is destroyed. This process causes ground-level concentrations to increase during the times of day when there is good mixing. As will be discussed later, the sunshine that warms the ground and causes mixing can also lead to the photochemical production of ozone, and to similar diurnal changes in ozone concentration at the surface.

Singh, et al. (1979), have also shown schematically typical annual variations in the natural tropospheric ozone burden. These are shown in Figure 2. At remote sites that are unaffected by anthropogenic emissions, the ozone concentrations tend to reach their maximum in the early spring. In general, the natural ozone falls somewhere in the shaded area marked A in the figure. Natural concentrations are at a minimum in the late fall or early winter. It is believed that the autumnal decline of ozone concentrations in these remote locations is caused by decreases in the injection of stratospheric ozone into the troposphere.

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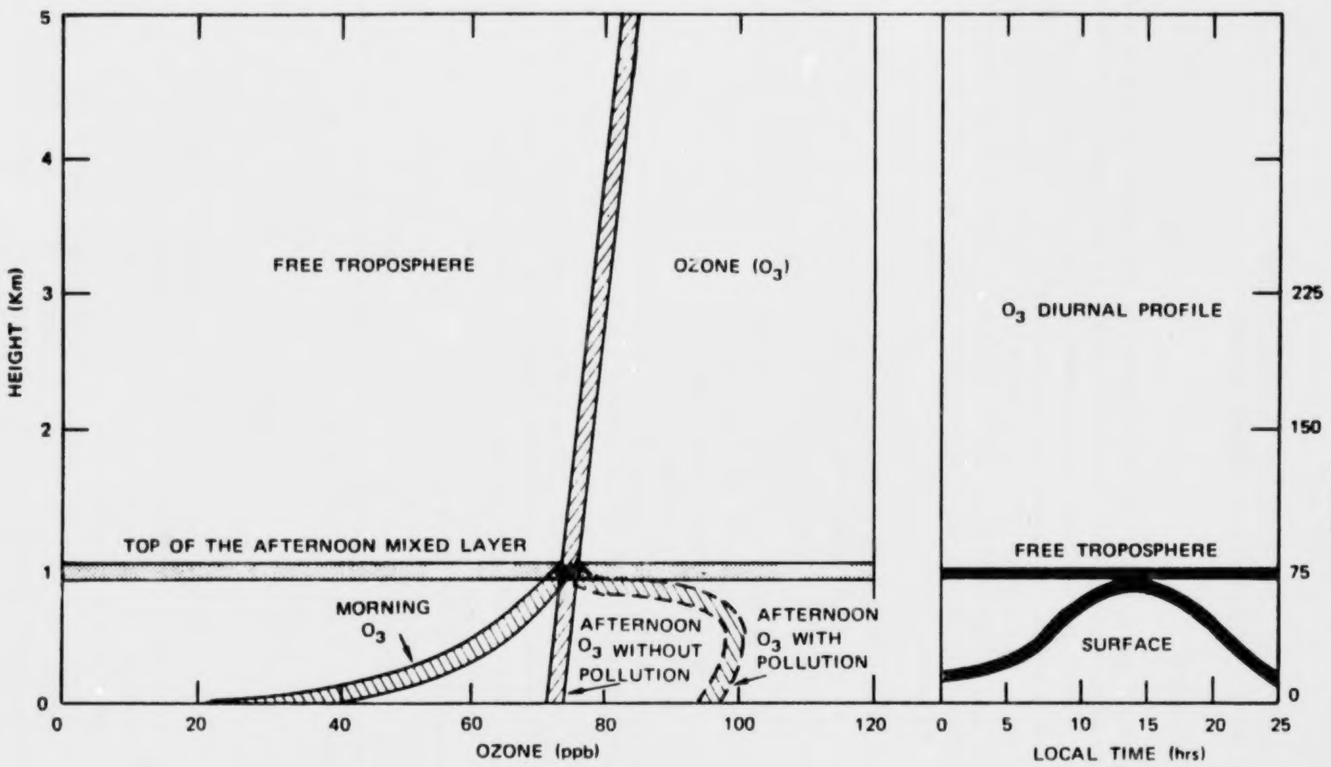

FIGURE 1 SCHEMATIC REPRESENTATION OF OZONE VARIATIONS AT THE SURFACE AND IN THE FREE TROPOSPHERE

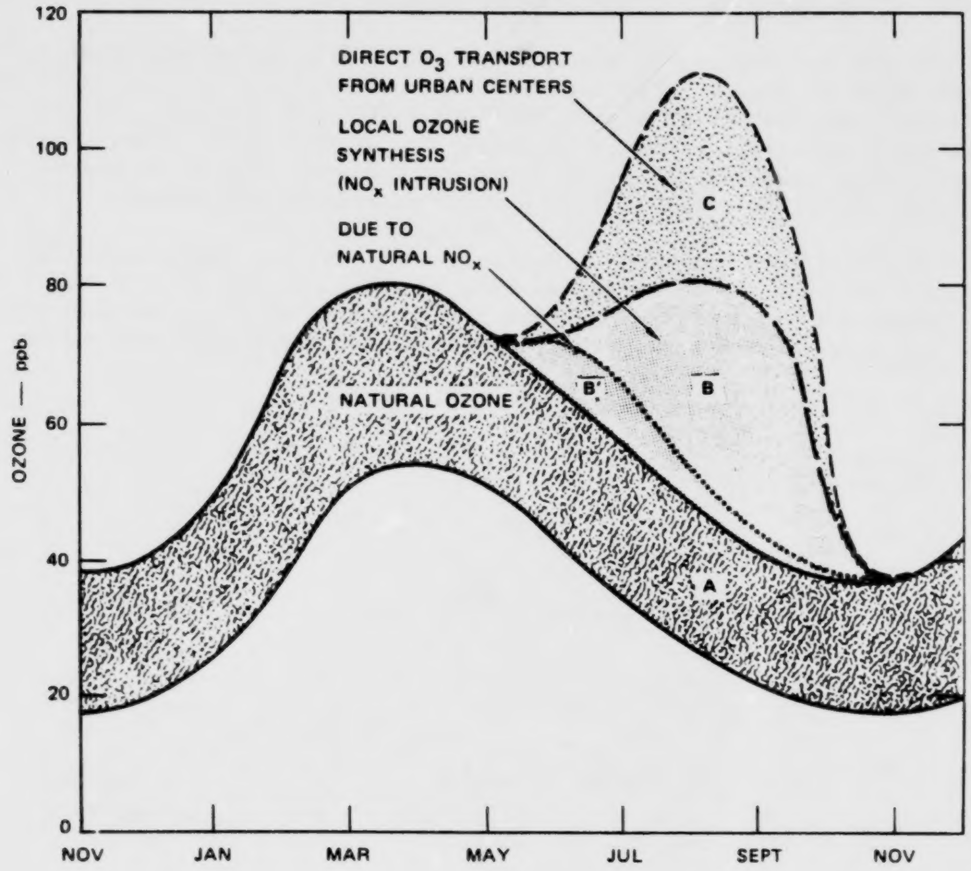

FIGURE 2 IDEALIZED OZONE VARIATIONS AT REMOTE LOCATIONS

Figures 1 and 2 indicate that if oxides of nitrogen are present, either from natural or anthropogenic sources, the diurnal and annual changes in ozone concentrations may be significantly affected. In the vicinity of urban areas, the effects may be further enhanced by the presence of reactive hydrocarbons. The next section deals with how the "natural" profile shown in Figure 1 for unpolluted atmospheres is modified by the emissions from cities.

2. Formation, Destruction, Transport, and Mixing of Ozone in the Vicinity of Cities

Before proceeding, it should be noted that profiles very similar to those shown in Figure 1 for unpolluted atmospheres can also be found in polluted atmospheres, if mixing has been sufficient to cause the pollutants to be distributed nearly uniformly in the vertical. Thus, we might expect ozone profiles in air entering any isolated city to be shaped somewhat like that shown in Figure 1 for unpolluted air masses.

Figure 3 is a schematic illustration of what one might expect to observe in the plume of emissions from a city. The top part of the figure shows the plume of hydrocarbons and oxides of nitrogen emitted during the morning rush hour. These emissions are reasonably well mixed

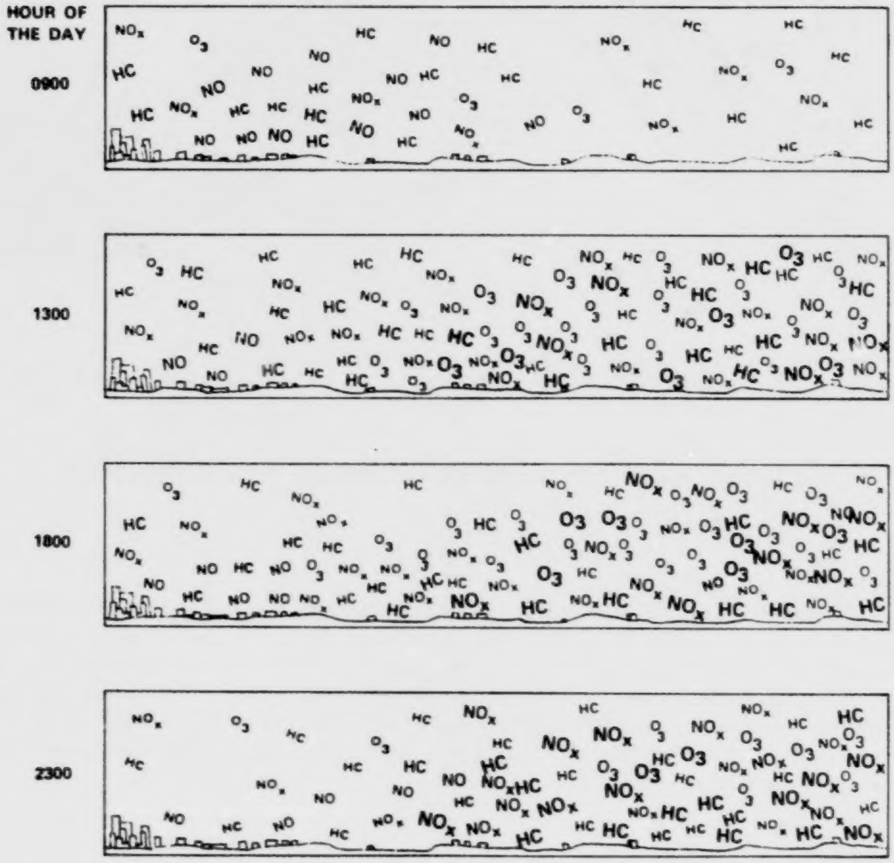

FIGURE 3 SCHEMATIC DIAGRAM OF THE TRANSPORT OF PRECURSORS, OZONE PRODUCTION, AND OZONE DESTRUCTION DOWNWIND OF A CITY

and have traveled some distance downwind of the city. At greater downwind distances, their densities are less because they have been diluted by mixing and also because they were emitted during the evening, when emission rates were much lower. There is some ozone scattered among the oxides of nitrogen and the hydrocarbons; at this morning hour, the ozone at the higher elevations is unlikely to have been produced by photochemical activity and probably reflects the "background" concentrations that have been advected into the city. The second panel of the figure shows the situation at about midday. The plume is dense with oxides of nitrogen and hydrocarbons for some distance downwind. Of considerable significance is the fact that much ozone has been produced by photochemical processes during the day. This ozone is distributed nearly uniformly in the vertical because of the strong daytime mixing. In general, the concentrations increase downwind of the city for some distance, a result of the time needed by the photochemical processes to produce the ozone. Eventually the production of ozone by the photochemical processes is offset by dilution, so concentrations fall off at greater distances from the city.

The third panel of Figure 3 illustrates the situation during late afternoon or early evening, when the oxides of nitrogen and the hydrocarbons have been uniformly mixed in the vertical. At this time, relatively dense concentrations occur for considerable distances downwind of the city. However, it should be noted that there are few ozone symbols scattered among the emissions that occurred later in the day (and are still close to the city), because photochemical processes are rather ineffective for producing ozone in the late afternoon. Another important characteristic of this diagram is the fact that ozone is confined to the upper parts of the plume at the greater downwind distances. This is caused by the formation of a stable layer near ground level in the late afternoon or early evening; the stable layer prevents mixing of ozone through the entire depth of the plume; the ozone that was in the lowest layers is destroyed at the ground and is not replaced by mixing from above.

The final panel of Figure 3 is an extension of the situation shown in the preceding panel. Concentrations of hydrocarbons and oxides of nitrogen are smaller near the city than they were earlier in the day because the emission rates have declined during the night. Ozone is not produced after sunset. Only the "background" ozone and that produced earlier in the day and advected far from the city are present. This accounts for the fact that very little ozone is found near the city. Farther downwind, in that part of the plume released earlier in the day when photochemical activity could take place, there is considerable ozone, but it is confined to the upper parts of the plume. Ozone in the lower parts of the plume has been destroyed at the surface.

The discussion to this point has shown that there are a limited number of processes contributing to the development of vertical ozone profiles. The relative importance of the processes varies with time of day, with meteorological conditions such as atmospheric stability, and with distance from the city. The three most important processes are destruction of ozone, production of ozone, and vertical mixing.

Destruction of ozone occurs mainly near the surface. If there is no nitric oxide (NO) present, destruction at the surface will occur fairly rapidly. The rapidity probably depends on the amount of surface area available for contact with the air, or as suggested by Vukovich (1973), the presence of natural agents that promote gas phase destruction of ozone. If nitric oxide emissions are present, as they generally will be from traffic and high-temperature combustion sources within the city, then the destruction of ozone will be very rapid. The presence of NO in plumes from large stationary sources such as power plants can also lead to the rapid destruction of ozone aloft, but in general the destruction of ozone in the free atmosphere away from the surface proceeds rather slowly.

The processes that operate to destroy ozone are active at all hours of the day and night, but the processes that operate to produce ozone from hydrocarbons (HC) and oxides of nitrogen (NO_x) are important only during the daytime. Another very important difference between the productive and destructive processes for ozone is the rate at which they occur. The important destructive processes occurring at the surface are quite rapid, while the productive processes tend to be slow by comparison For this reason, the destructive effects associated with a city's NO emissions will be observed over the city and in its immediate environs, while the ozone production that will result from those same emissions will take place some distance downwind. Ludwig and Shelar (1978) have estimated that the maximum concentrations of locally produced ozone will be found downwind of a large city at a distance that corresponds to a travel time of five to seven hours from the upwind edge of the urban area. Although the maximum ozone concentrations generally occur within a few tens of kilometers of the city, the ozone produced by emissions from a city can be detectable much farther downwind. Discernible ozone plumes generated by emissions from East Coast cities have been observed well over 100 km downwind of those cities (e.g., Cleveland, et al., 1976; Zeller, et al., 1977; Spicer et al., 1977).

Vertical mixing is the third factor that influences the nature of the vertical distributions of pollutants, especially ozone, in the vicinity of cities. Mixing causes the pollutants to be transported vertically to and from the sinks and sources. For the oxides of nitrogen and the hydrocarbons, there is a source at the surface. For ozone, the surface is a sink; the source of ozone tends to be rather diffuse and coincides with the volume occupied by the oxides of nitrogen and the hydrocarbons. Obviously, if mixing is weak, the effect of the source or sink will not extend very far into the overlying atmosphere, and the gradients in the immediate vicinity of that source or sink are apt to be quite large. If the mixing is very vigorous, then the effect of the source or sink will extend to much higher levels, and the gradients are apt to be much more uniform.

There is one other important process to be considered in analyzing vertical profiles in the vicinity of cities--the horizontal transport process. Transport, of course, determines where the air entering the city has come from, and, indirectly, the pollutant burden that it is carrying with it as it enters the city. It also determines where the air goes after it leaves the city. The rate at which the air is moving--i.e., the resultant wind speed--determines the volume of air into which the emissions are mixed and hence their concentration. The wind speed also determines how far the air travels downwind of the city during the time the photochemical reactions producing ozone are operative. There are also relationships between wind speed and vertical mixing; rapid air movement over a rough surface can induce mechanical turbulence. High wind speeds near the surface are also an indication that momentum is being transferred downward by vertical mixing.

B. Types of Vertical Ozone Profiles

The processes discussed in the preceding section can interact in different ways to produce a variety of vertical ozone profiles. The relative strength and vertical extent of mixing, the relative importance of the sources and sinks, and the time over which all the processes operate will contribute to the development of the vertical pollutant profile. It was anticipated that a taxonomy of vertical pollutant profiles might be developed and that it might be possible to relate the different types of profile within that taxonomy to different kinds of interrelationships among the processes that produce the profiles. With this in mind, the vertical profiles from the four major study areas were examined to see if a reasonable classification system could be developed.

Figure 4 shows the classification system that evolved from this effort. Six basic types of ozone profile were commonly observed. To some extent, these categories have evolved from earlier work presented by Johnson and Singh (1977). However, their work focused on profiles of the type found in the last two categories of Figure 4. The classification system discussed below is more general than their work. (It should be noted that the height and concentration scales that are used in Figure 4 are for illustrative purposes only. The values used are typical, but observed conditions can differ widely.) Types A and B are closely related to the "background" conditions shown earlier in Figure 1. Type A gives little evidence of any nearby anthropogenic effects. Such a profile arises when mixing is very thorough. The small gradients near the surface are an indication that either the mixing is vigorous or the surface sink is weak. The uniformity of the profile in the upper level is an indication that sufficient time has elapsed since any ozone forming precursors were introduced so that the precursors and ozone have been thoroughly mixed through a very deep layer.

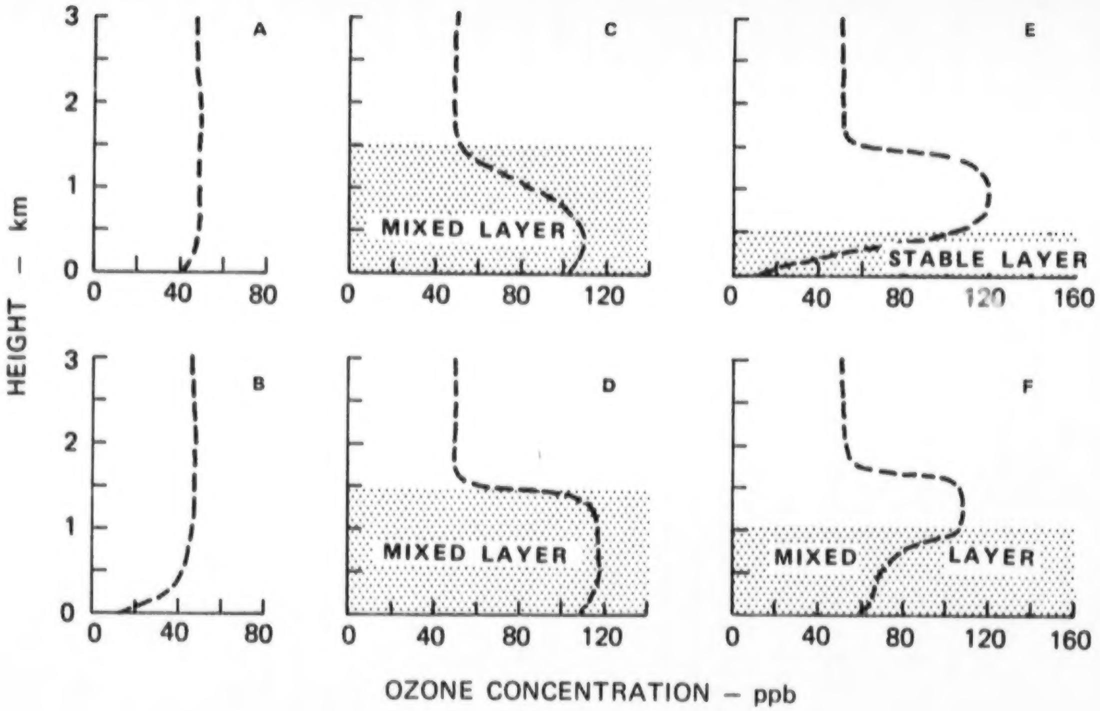

FIGURE 4 SIX TYPES OF VERTICAL PROFILE

The Type B profile in Figure 4 is related to the Type A profile in one of two ways. Either the magnitude of the sink at the surface is greater than for the Type A profile, or the vertical mixing, especially in the lower layers, is weaker. Weaker vertical mixing will generally result from formation of a stable layer near the surface. A stable layer will form when the air is cooled from below. Typically, this will occur by radiative cooling in the late afternoon and evening. It can also occur when air is advected over a cooler surface such as water (see, for example, Lyons and Cole, 1976).

The most common way in which a surface ozone sink can be enhanced is by the introduction of NO. Thus, a vertical ozone profile of Type B can evolve from a Type A when lower layers of the atmosphere become very stable or when the air passes over a source of NO, such as a city, or by some combination of these two causes.

The remaining four types of profiles show the effects of the introduction of anthropogenic pollutants, and hence they might be considered to be "urban" or "downwind" types. The major differences between the conditions that would cause a Type C profile and those that would cause a Type D are the elapsed time since the original emissions were released and the vigor of the mixing during the intervening time. For a profile of Type C, mixing has not proceeded to the point where the pollutants are uniformly distributed through the mixing layer, as they are for Type D. In both cases, the slight increase with height just above the surface shows the effect of the surface sink for ozone. To a large extent, the sink is offset by the vertical mixing, but not completely. If profiles were shown for pollutants that are not destroyed at the surface, there would not be the gradient in the lowest layers. For primary pollutants, emitted directly into the atmosphere, Type C or D profiles could occur at almost any time of day, but for ozone they are most likely to occur in the afternoon. This is because sunshine is required to produce the ozone, and mixing (caused by warming of the surface) is required to offset the destruction at the surface.

One can imagine a profile of Type D evolving to one of Type E in exactly the same fashion as a profile of Type A evolves to Type B. In one case, a stable layer develops near the surface, as shown in Figure 4, so that surface destruction or gas phase destruction by natural agents (Vukovich 1973) are not offset by vertical mixing. The second way that the types E or B profiles evolve is when the ozone-laden air passes over an area where the surface destruction of ozone is very strong, such as a city with heavy NO emissions. Thus, a Type E profile could occur in at least four different situations:

- Downwind of a city at night, when a stable layer has formed by cooling of the surface, especially if natural destructive agents are present.
- In air that has passed over a cool surface, such as the sea, after it has left the city.

- In air that has left one city but is passing over another with strong NO emission.
- In air that is recirculating over the city of origin or continuing to pass over that city, if the city is very large.

Type F profiles can result from several different processes. The most common requires several steps. Johnson and Singh (1977) have described a sequence of events that leads to a profile of Type F. Figure 5, from their report, shows the situation in which air moves from an urban area to a rural area. In the first panel, there is a Type D profile that has resulted from photochemical reactions involving precursors distributed throughout the mixing layer. At night, this profile evolves into the Type E profile shown in the center panel, as the ozone in the stable layer near the surface is destroyed. The final section of Figure 5 shows conditions on the following day; in this example, the mixing depth is not as great as it was on the preceding day. Because the mixing depth is less on the second day, only the lower levels of the ozone layer aloft are eroded and mixed downward. This leaves intact the greater ozone concentrations at the higher altitudes.

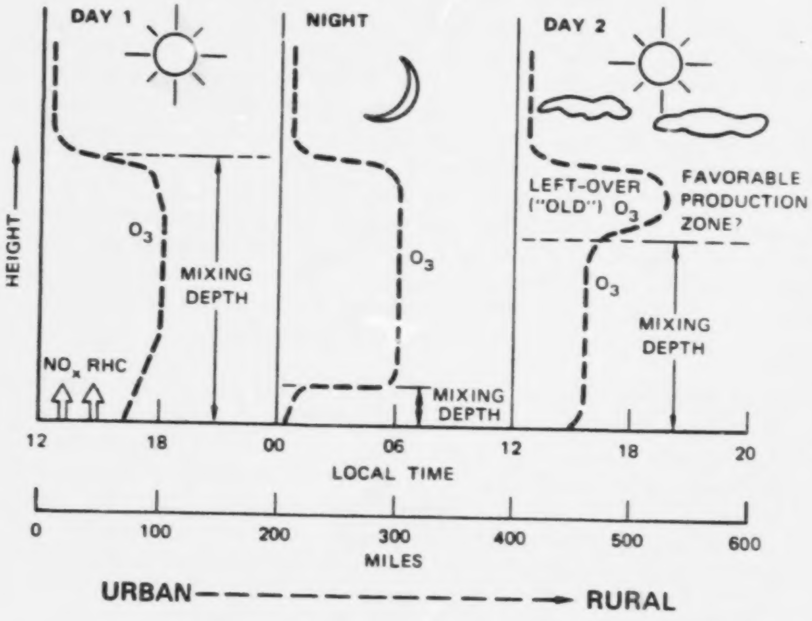

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FIGURE 5 TYPICAL DIURNAL EVOLUTION OF THE VERTICAL OZONE PROFILE AS AIR MOVES FROM URBAN TO RURAL AREAS

Johnson and Singh (1977) point out that reduction in the depth of the mixed layer from one day to the next can occur for a number of reasons. For example:

- Reduced insolation (from increased cloudiness), causing less pronounced convection.
- Increased surface moisture that reduces transfer of sensible heat and also leads to weaker convection.
- Passage of the air from a warmer to a colder surface.
- Large scale subsidence.

Changes in the mixing depth are not unusual from day to day. If the depth of the mixing layer decreases from one day to the next, it can leave a relatively concentrated layer of ozone isolated aloft and result in a profile of Type F. If the mixing depth increases again on subsequent days, that layer will tend to be mixed more uniformly and the resulting profile will evolve toward Type A, completing the cycle.

As noted before, the Type F profile can result from processes other than that just described. For example, Edinger (1973) suggested that elevated layers of pollution are formed in the Los Angeles Basin when polluted air near the ground moves up heated mountain slopes at the northern part of the Los Angeles Basin, and then moves out from the mountains horizontally within the inversion that commonly caps the marine air in Los Angeles. The presence of polluted layers aloft in the Los Angeles area has been observed frequently (e.g., Blumenthal et al., 1974; Johnson and Ruff, 1975). This report does not give much attention to this particular mechanism for the formation of profiles of Type F, since it appears to have rather unique geographical requirements. It is probably necessary to have both mountainous terrain, to deflect the airflow, and a very strong inversion aloft. Los Angeles is among the few places that have the combination of a frequently occurring subsidence inversion (in association with the Pacific anticyclone) and the requisite terrain.

There is yet another way that profiles of Type F can be formed. This is through the introduction of photochemical precursors into a stable layer aloft. Blumenthal et al. (1974) have also observed this phenomenon in the Los Angeles area. While this mechanism produces Type F profiles for a primary pollutant, such as NO_x and HC, it results initially in a very different profile for ozone. The high concentrations of NO in a plume will severely reduce the ozone concentrations within the plume. This will produce a vertical profile that is a complement of Type F profile. There will be a layer aloft with less ozone concentration. However, if there is sufficient sunshine, the increased concentrations of NO_x and HC will result in corrrespondingly increased concentrations of ozone after some time has elapsed. Although this mechanism can occur in almost any geographical area, its consequences are likely to be of rather limited extent. If the plume is injected into a layer sufficiently stable that it will maintain its identity for a prolonged period of time, that same stability will tend to limit the horizontal extent of the plume. For this reason, we have chosen not to deal with this phenomenon in any great detail.

The system described above for classifying vertical pollutant profiles provides a basis for examining observations in the vicinity of cities. Of course, the ultimate objective is to use this classification scheme for extrapolating surface observations of ozone and other pollutants to higher elevations. Profiles of Types A and D certainly should allow this to be done. The question becomes, how does one recognize, from ground based pollution measurements and conventional meteorological observations, just when such profiles are likely to exist? The observed profiles from several cities will be examined later in an attempt to answer this question.

C. Other Considerations Concerning Ozone Profiles

The classification system for vertical profiles (discussed in the preceding section) is only one of the important factors that need to be considered. Other important factors include

- Time of day
- Depth of the mixing layer
- Atmospheric stability
- Temperature and cloud cover
- Winds
- Location relative to the city.

Time of day is important because it provides a first estimate of mixing conditions and of the strength of photochemical processes that might be producing ozone. Photochemical processes occur only in the daytime. They require sunshine and have also been found to depend on temperature; this is one of the reasons some consideration should be given to temperature and cloud cover.

The mixing depth and the presence of stable layers will generally determine at what altitudes the major transition points of the different types of pollutant profile will occur. Obviously, mixing depth will play an important role in any attempt to define vertical profiles of pollutants. Atmospheric stability will determine the vigor of the mixing process and influence the nature of the profile. Atmospheric stability is related to cloud cover, wind speed, and time of day, a fact that contributes to the inclusion of those items on the list of important factors.

Winds, of course, determine where the pollutants are carried (direction) and the volume of air into which they are mixed (speed)--hence, how much they will be diluted. It is essential to know the wind direction in order to define whether a location relative to the city is upwind, downwind, or to one side. It should be evident from the discussion in the preceding section that location relative to the city is an important determinant of vertical ozone profile type.

III OBSERVED VERTICAL PROFILES

A. General

An attempt has been made in the following sections to group the examples from each of the primary study areas along the lines discussed in the preceding sections. The first point that should be made is that the classifications and the groupings are often based on subjective judgments. Sometimes the vertical extent of the measurements was not sufficient to determine the mixing depth or to adequately classify the character of the vertical profile. Not all hours of the day are represented. In spite of the shortcomings, there is an encouraging consistency and orderliness to the results.

Each of the following sections includes a tabulation of the vertical profiles considered. The majority of those profiles for the primary study areas are displayed in this report. An attempt has been made to bring together as much information as possible in the graphical displays. In general, the displays include the vertical profiles and maps of the distribution of ozone at ground level. An indication of the wind direction is included to define the location relative to the city at which the sounding was made. The primary emphasis has been on ozone, and that pollutant is always included in the displays. The Los Angeles, St. Louis, and Washington data generally include nephelometer readings (Bscat). Vertical profiles of temperature usually accompany the ozone profiles. Frequently, dew point temperature is also available. Unfortunately, reliable NO_x and hydrocarbon measurements were not generally available.

Finally, it should be noted that the formats of the graphical presentations differ somewhat from one section to the next. There are two reasons for this. First, the available data differed from city to city and so the displays must reflect that fact. Second, when data were not available in computer-compatible form, but had been graphed, we made use of the preexisting graphical displays. The text calls attention to differences in display and the reasons for those differences, so it should cause the reader little trouble.

B. Primary Study Areas

1. St. Louis

a. Background

By far the most numerous data are available from the St. Louis area. Several days suitable for analysis were selected from the larger body of data. Mage et al. (1978) provided a list of days on which special helicopter missions had been flown during the Regional Air

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Pollution Study (RAPS) in St. Louis. This list was compared with a list of days during 1976 when high ozone concentrations were observed in the St. Louis area. The latter list was provided by the project officer, Mr. E. L. Martinez. Several of the days when special helicopter missions had been flown and relatively high ozone concentrations had been observed were selected for intensive study and the data were obtained. Some days with very high ozone concentrations were not selected for analysis, because those dates were not listed among the days when special helicopter missions had been flown. However, some of those days may have helicopter data of a more routine nature that was collected, but not tabulated, by Mage et al. (1978). Table 1 summarizes the 94 vertical profiles of ozone concentration in the St. Louis area that were analyzed during the course of this project. The times given in the table are Central Standard Time (CST) and refer to the approximate time at which the vertical profile was completed. The mixing depths are given in kilometers above sea level; the approximate elevation in the St. Louis area is 0.15 km. The atmospheric stability class, as shown in Table 1, was derived from information given on the surface weather charts. The classification system is the one suggested by Pasquill (1961) and Gifford (1961); Turner's (1969) algorithm was used. The wind speeds and directions shown in Table 1 were estimated from the surface weather maps.

The vertical profiles were taken at a limited number of locations, which are shown in Figure 6. In Table 1, the profiles taken in the vicinity of Smartt Field are designated with location number 131. Wherever possible, the vertical profiles were taken directly above one of the stations in the RAPS network. In those cases, the profile is identified by the number of the station over which it was taken. At some locations, it was not feasible to fly the helicopter at low levels directly above a station so an alternative site was chosen nearby. In those cases, the profile location is designated with a number that corresponds to the nearest RAPS station followed by the letter (H). The classification of the location of a profile relative to the city is determined by the extent to which that profile might have been affected by the city. If the profile was taken upwind of the city or to one side of it, then the first column in Table 1 under the heading "Location Relative to the City" is checked. The second column is checked when the profile was taken in the heavily urbanized part of the city, and the third column when the profile was clearly taken downwind of the city. In general, an attempt has been made to take into account changes of wind direction that might have caused air flow from the city to reach the place where the profile was taken, even though the wind direction at the time of measurement might indicate that that site was uninfluenced. In some cases, it was impossible to determine whether a profile had been influenced by recent emissions from the city; in those cases, the last column was checked.

The ozone profiles were categorized according to the system already discussed. It is important to remember that the classifications are subjective and that there are inevitably some profiles whose classification

Table 1

SUMMARY OF OZONE PROFILES STUDIED FROM THE ST. LOUIS AREA

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 6)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760719	0621	0.5	D	5	180	131	x				E	55	75
	0721	0.5	D	5	180	124	x				E	65	90
	0724	0.5	D	5	180	131	x				E	55	70
	0750	0.4	D	5	190	102		x			E	40	60
	0801		D	5	190	103H				x	D	90	100
	0814	0.4	D	5	190	106H		x			F	40	65
	0821	0.5	D	5	200	124	x				A	80	85
	0831	0.4	D	5	200	105H	x				A	70	85
	0839	0.5	D	5	200	102		x			F	60	70
	0849	0.5	C	5	200	103H	x				A	75	85
	0850		C	5	200	102		x			F	60	70
	0901		C	5	200	106H		x			F	50	70
	0911		C	5	200	106H		x			F	50	70
	0912		C	5	200	105H	x				F	80	90
	0926	0.5	C	5	200	105H	x				F	80	90
	0938	1.3	C	5	190	131			x		D	95	100
	0938	1.4	C	5	190	102		x			F	75	70
	0947	1.4	C	5	190	103H	x				A	85	95
	0959	1.4	C	5	190	106H		x			D	75	85
	1011	1.4	C	5	190	105H	x				A	80	95
	1034	1.4	C	5	190	131	x				A	100	100
	1257	1.8	C	5	170	131			x		D	110	105
	1315	1.8	C	5	170	121			x		D	120	120
	1338	1.8	C	5	170	115	x				D	100	95
760723	0442	0.4	D	2.5	240	131	x				E	5	30
	0501	0.4	D	2.5	240	131	x				E	10	35
	0707	0.4	D	2.5	240	103H			x		F	20	45
	0741	0.3	C	3	240	131	x				A	60	60
	0842	0.6	D	5	240	131	x				A	70	70
	1128		C	7.5	240	131	x				A	75	70
	1320		C	7.5	240	131	x				A	80	70

Table 1 (Continued)

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 6)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760729	0619	0.3	D	4	250	131	x				E	0	20
	0639	0.5	D	4	270	131	x				E	5	15
	0648	0.5	D	5	290	131	x				E	5	20
760730	0733	0.6	C	4	180	124	x				E	60	75
	0800	0.4	C	4	180	102		x			F	30	30
	0807	0.3	C	5	180	103H			x		F	35	35
	0821	0.4	C	3.5	190	106H		x			F	30	45
	0834	0.5	C	3.5	190	105H		x			F	40	60
	0844	0.5	C	3.5	190	102		x			F	30	50
	0902	0.5	C	3.5	190	131				x	A	45	55
	0915	0.5	C	3.5	190	103H			x		A	60	65
	0925	0.5	C	3.5	240	106H		x			F	80	55
	0952	0.5	C	3.5	240	131	x				A	90	80
	1030	0.7	B	2.5	280	131	x				A	100	80
	1139	0.8	B	2.5	260	131	x				A	90	75
760803	0608	0.4	D	0	-	131				x	F	20	30
	0637	0.4	C	2	80	123	x				F	10	35
	0657	0.3	B	2.5	80	122	x				F	15	30
	0707	0.3	B	2.5	80	103H	x				F	20	35
	0718	0.4	B	2	70	106H		x			F	10	15
	0733	0.4	B	2	70	105H				x	F	25	30
	0744	0.3	B	2	60	102	x				F	20	25
	0752	0.3	B	2	60	103H				x	F	20	25
	0802	0.3	B	2	60	106H	x				F	15	15
	0813	0.3	B	2.5	80	105H	x				F	20	30
	0841	0.4	B	3	120	131	x				F	25	30
	0839	0.8	A	2	90	131	x				A	60	60
	1058	1.5	A	1.5	90	131	x				A	60	65
	1115	1.6	A	2.5	90	102	x				A	80	70
	1122	1.7	A	2.5	90	103H	x				A	75	75
	1125	1.7	A	2.5	90	123	x				A	80	80

Table 1 (Concluded)

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 6)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760803	1138	1.6	B	3	90	105H			x		C	70	80
	1145	1.6	B	3.5	90	102		x			A	70	75
	1151	1.7	B	3.5	90	103H	x				A	75	75
	1153	1.7	B	3.5	90	102		x			A	85	80
	1159	1.6	B	3.5	90	103H	x				A	85	80
	1201	1.6	B	3.5	90	106H		x			A	90	75
	1210	1.6	B	3.5	80	106H		x			A	90	80
	1214	1.6	B	3.5	70	105H		x			A	80	75
	1227	1.6	B	3.5	60	102		x			A	90	85
	1234	1.6	B	3.5	50	103H	x				A	90	80
	1240	1.6	B	3.5	50	123	x				A	95	85
	1243	1.6	B	3.5	40	106H		x			A	100	90
	1313	1.6	B	3.5	40	131	x				A	95	80
	1549	1.5	B	2	330	102		x			D	120	130
	1556	1.5	B	2	330	103H			x		D	100	120
	1607	1.5	B	2.5	320	106H		x			E	110	135
	1619	1.6	B	2.5	320	105H			x		D	100	110
	1631	1.7	C	3	310	123	x						145
	1645	1.8	C	3	300	106H		x			E	100	120
	1745	1.8	D	2	30	131				x	A	60	70
760804	0743	0.4	C	3.5	190	131	x				F	25	40
	0831	0.5	B	2.5	210	124	x				A	40	50
	0856	0.6	B	2	220	102		x			F	60	75
	0903	0.6	B	2	220	103H			x		C	60	60
	0924	0.6	B	3	230	105H			x		D	55	75
	0933	0.6	C	3	230	102		x			D	75	85
	0941	0.8	C	3.5	240	103H			x		D	75	75
	1001	0.9	C	4	240	105H			x		D	75	80
	1027	1.0	C	3.5	230	131	x				D	75	70
	1258	1.6	C	3.5	240	131	x				D	90	100
760812	0629	0.5	D	4.5	160	131	x				B	25	70
	0841	0.5	C	4.5	240	131	x				A	70	75

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

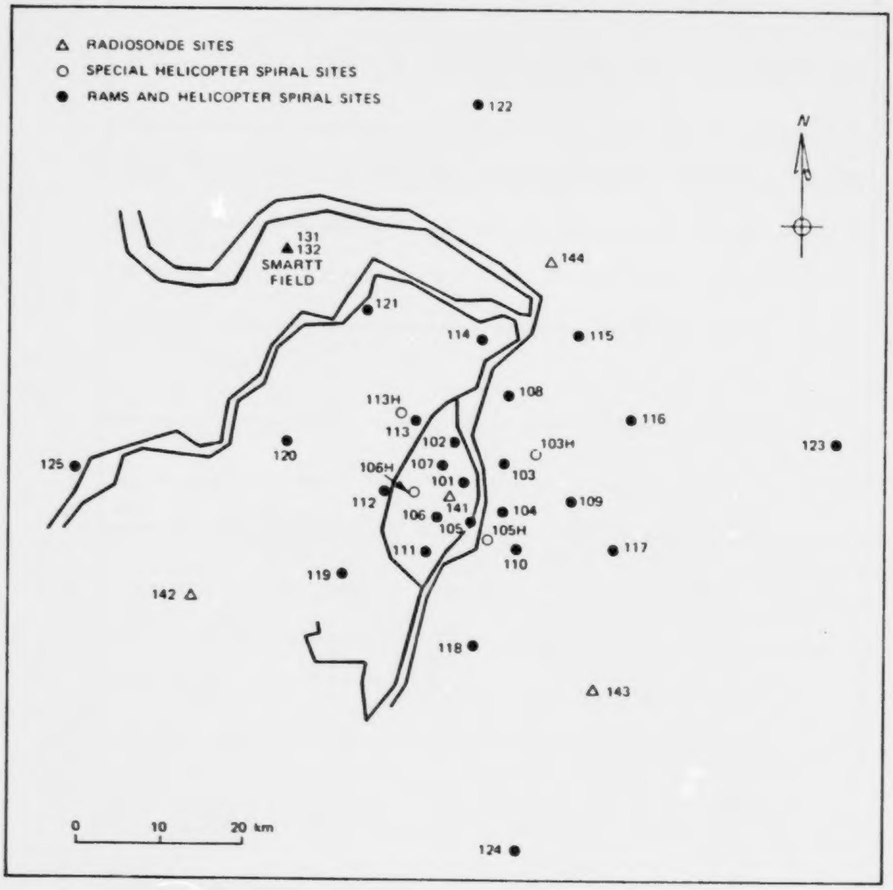


FIGURE 6 MONITORING AND HELICOPTER SOUNDING LOCATIONS IN THE ST. LOUIS AREA

is ambiguous. The last two columns of Table 1 give the estimated ozone concentrations at the surface and aloft. The surface concentrations were estimated from objective isopleth analyses of data collected at the RAPS stations. These objective analyses involve some smoothing, which should minimize localized, unrepresentative influences that might be reflected in the data from a single station. The concentrations shown in the last column of the table are approximate averages of the concentrations through the mixed layer. Of course, concentrations above the mixed layer might be considerably higher, as in the case of ozone profiles of Type F, or considerably lower, as in the case of ozone profiles of Type D.

The available sample of ozone profiles from St. Louis is heavily biased toward those taken during the morning hours. Over three-quarters of the cases shown in Table 1 represent hours between 0600 and noon. As a result, all the stability classes represented are neutral (Class D) or one of the unstable class (A = extremely unstable, B = moderately unstable, C = slightly unstable). More afternoon profiles are available from some of the other cities, but there are few nighttime profiles available anywhere. This seems to be one of the serious shortcomings of the available data set. Table 2 summarizes the frequency with which different types of ozone profiles are represented in the St. Louis data set. Obviously this is not necessarily the frequency with which these categories occur in the St. Louis area in general, since the data set is biased toward high ozone concentration, toward the morning hours, and probably toward fair weather conditions conducive to flying. The table shows that the ozone profile Types A and F were most frequently observed, but appreciable numbers of Types D and E were also found. The scarcity of Type B profiles probably reflects the scarcity of nighttime observations.

Table 2

RELATIVE FREQUENCIES OF OZONE
PROFILE CATEGORIES IN THE
ST. LOUIS DATA

Profile Type	Relative Frequency (percent)
A	38%
B	1
C	2
D	15
E	14
F	30

b. Examples

This section gives examples of vertical profiles and the corresponding distribution of ozone concentrations near the surface in the St. Louis area. Figure 7 shows the conditions that prevailed on the morning of July 19, 1976. Five vertical ozone and nephelometer profiles, measured between 0814 and 0849 CST, are shown. Where more than one profile was measured at nearly the same time and in the same location, double lines are shown. The locations at which the various profiles were measured are indicated on the map at the left center of the figure. This map also shows isopleths of ozone concentrations determined from the RAPS data for the hour in which the profiles were measured. The arrows indicate wind directions measured at the RAPS stations; the lengths of

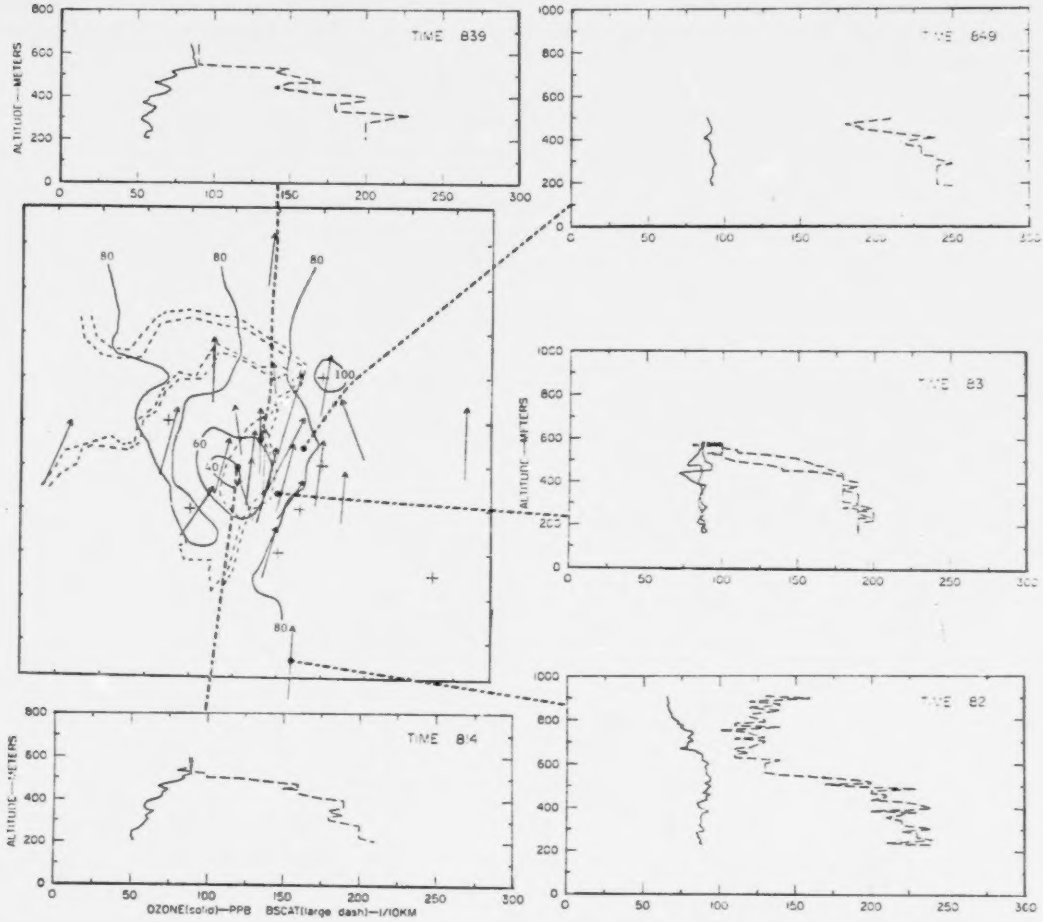


FIGURE 7 ST. LOUIS OZONE CONCENTRATIONS ON THE MORNING OF JULY 19, 1976

the arrows equal one hour's travel distance at the measured speed. The location of the rivers and the most heavily urbanized part of St. Louis are marked by dashed lines.

On the preceding day, St. Louis had been near the center of a large high-pressure system. On this morning, the high-pressure system was somewhat to the east, but St. Louis was still in the western part of the anticyclone and heavily influenced by the same system. There is every indication that considerable accumulation of ozone occurred within the high-pressure system; concentrations in excess of the then existing National Ambient Air Quality Standard (NAAQS) of 80 ppb were found throughout the area outside the city itself. Within the city, the emissions of NO reduced ozone concentrations to less than 60 ppb. The profile taken south, and upwind, of the city at 0821 shows that concentrations of 80 ppb were present through a considerable depth of the atmosphere. The profiles taken to the side of the city at 0831 and 0839 also show that concentrations of 80 ppb or more extended from the surface upward for some height. All these profiles have been classified as Type A because the high concentrations extended through the top of the mixed layer; this is assuming that the upper boundary of the mixed layer was accurately marked by the abrupt decline seen in nephelometer (aerosol concentrations) readings. However, there is some evidence that the ozone concentrations begin to drop at higher levels, and so there may be some justification for classifying these as Type D profiles. The influence of the city is clearly seen in the profiles taken at 0814 and 0839. The upper parts of these profiles are very similar to those taken outside the city, but the lower parts show concentrations that are much below those outside the city. Both these profiles have been classified as Type F. Ozone concentrations above the mixed layer reflect the effects of earlier accumulations of precursors and photochemistry and thus are higher than the concentrations of ozone within the mixed layer. Obviously, the emissions from St. Louis had not had time to produce ozone concentrations as great as those arising from the preceding day, and in fact have reduced those concentrations at the lower altitudes over the city. The shape of the profiles are characteristic of Type F profiles.

Figure 8 shows conditions in the St. Louis area on the morning of July 23, 1976. Three of the profiles were taken at Smartt Field, northwest of St. Louis at different times during the morning. The fourth profile was measured at 0707 CST, just downwind of the city; that profile, along with the corresponding nephelometer and temperature profile, is shown at the top right of Figure 8. There is evidence of ozone preserved in the stable air shown in the temperature profile at about 400 m. The ozone profile gives evidence of considerable destruction of ozone by the NO emissions from the city below that same height. These factors have led to a Type F classification. The other three profiles in Figure 8 show the evolution of ozone profiles during the period when the surface stability was wiped out by the onset of solar heating. The temperature profile measured at 0501 shows a strong, surface-based stable layer. Correspondingly, the ozone profile shows a sharp gradient connecting concentrations of 60 ppb or more at a height of less than

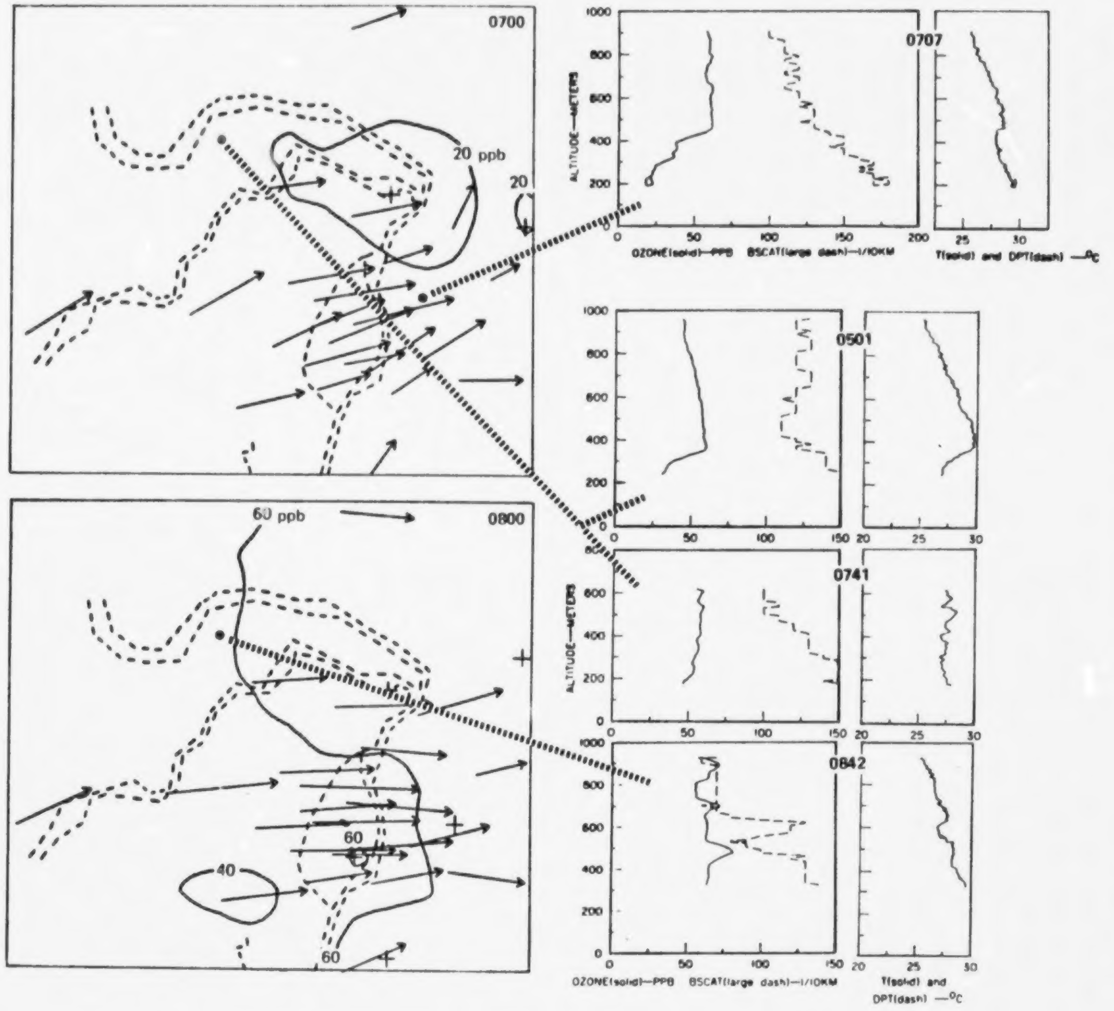

0700
20 ppb
20
0800
60 ppb
60
40
60
0707
0501
0741
0842
ALTITUDE—METERS
OZONE(solid)—PPB BSCAT(large dash)—1/10KM
T(solid) and DPT(dash) —°C

FIGURE 8 ST. LOUIS OZONE CONCENTRATIONS ON THE MORNING OF JULY 23, 1976

400 m, with concentrations less than 20 ppb at the surface. By 0741 CST, the temperature profile shows that temperature decreased with height up to about 300 m. This evidence of mixing is supported by evidence in the ozone profile, which no longer had the very low concentrations in the lower layers. Finally, by 0842, the concentrations of ozone in the lowest layers had increased still further. Some rather interesting features are shown in the upper parts of the nephelometer and ozone profiles. For example, at about 600 m, the nephelometer profile shows a sharp peak, while there is a minimum in the ozone profile. This suggests the presence of a distinct plume confined by the stable layer evident in the temperature profile at about the same height. The plume appears to contain increased amounts of particulate material and reduced amounts of ozone, probably caused by the presence of NO in the same plume.

Figure 9 shows two vertical profiles taken later in the day on July 23, 1976, again at Smartt Field. By this time, mixing had progressed to the point where concentrations were virtually uniform with height throughout the depth of the vertical profile. Since the measurements did not go above the depth of the mixing layer, it is not possible to say if the uniformity of concentration continued above that height. However, the profiles were classified as Type A on the presumption that the concentrations of about 60 or 70 ppb would not be unreasonable, throughout a fairly substantial depth of the atmosphere, in a high-pressure area such as was found to the south and east of St. Louis on the morning of this day. By the time represented by the two maps in Figure 9, it is apparent that precursors from St. Louis were causing a build-up of concentrations at the surface in areas downwind of St. Louis.

Figure 10 shows conditions in the early morning hours of July 29, 1976. The two ozone profiles shown are classified as Type E, although they might well have been classified as Type B. Inversion or isothermal lapse rates are present in the lowest few hundred meters of the atmosphere. As a consequence, ozone destruction at the surface reduced concentrations to near zero values in the lowest layer; there was insufficient mixing from above to offset the destruction. The reason for categorizing these as Type E rather than Type B profiles is found in the nephelometer profiles. The nephelometer profiles show evidence of a strong pollution layer aloft. It has been presumed that high ozone concentrations were associated with this evidence of higher pollution, rather than background levels, as would be the case with Type B profiles. Obviously, this is a subjective choice, and the interpretation is complicated by the fact that there was a stationary front in the immediate vicinity of St. Louis at this time, so the nephelometer readings may well reflect something other than pollution, such as the presence of some condensation. The general flow pattern at the two times shown in the figure indicates that there was a wind shift such as might be associated with the passage of the front.

Figure 11 shows five profiles taken in the vicinity of St. Louis between about 0730 and 0830 CST on the morning of July 30, 1976.

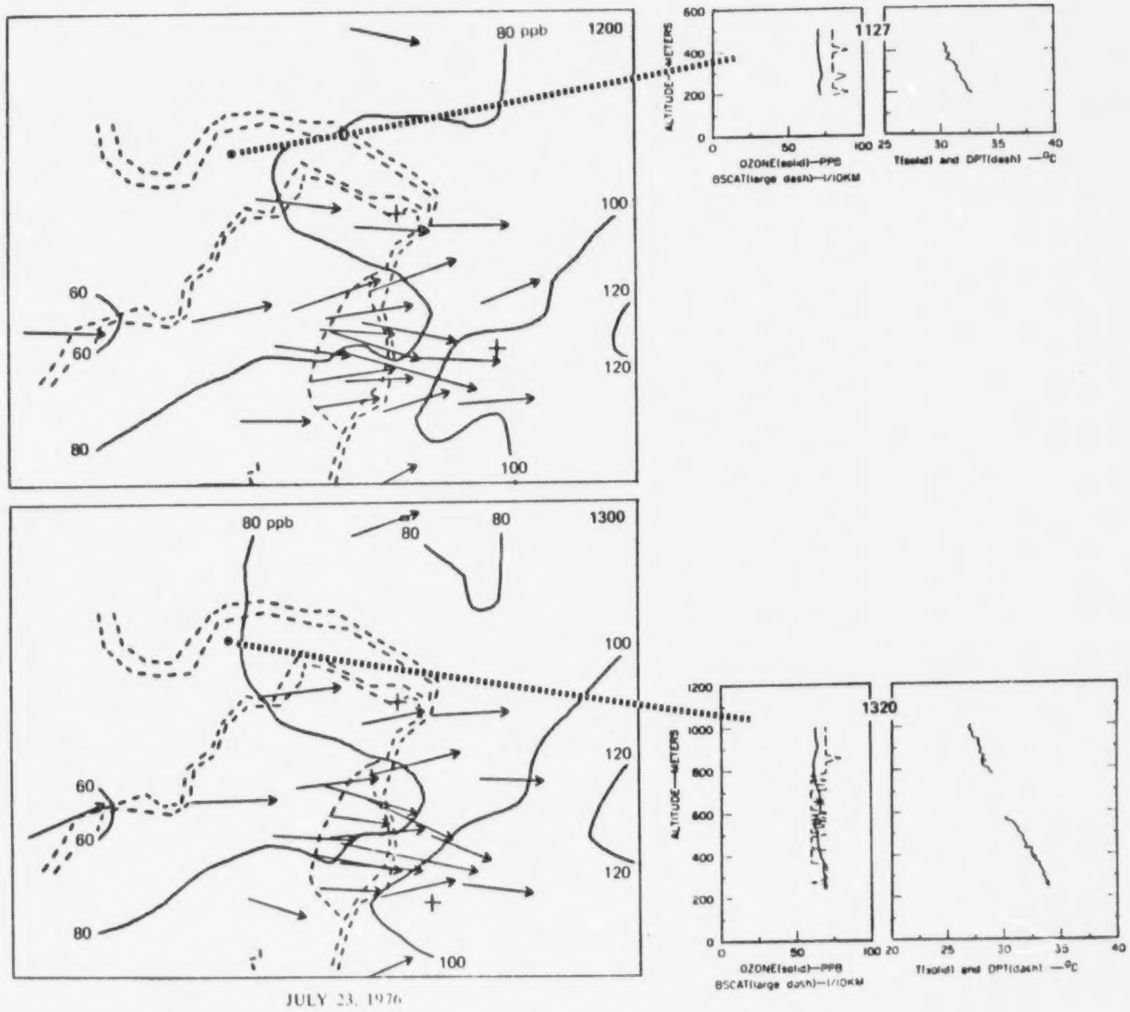


FIGURE 9 ST. LOUIS OZONE CONCENTRATIONS AROUND MIDDAY ON JULY 23, 1976

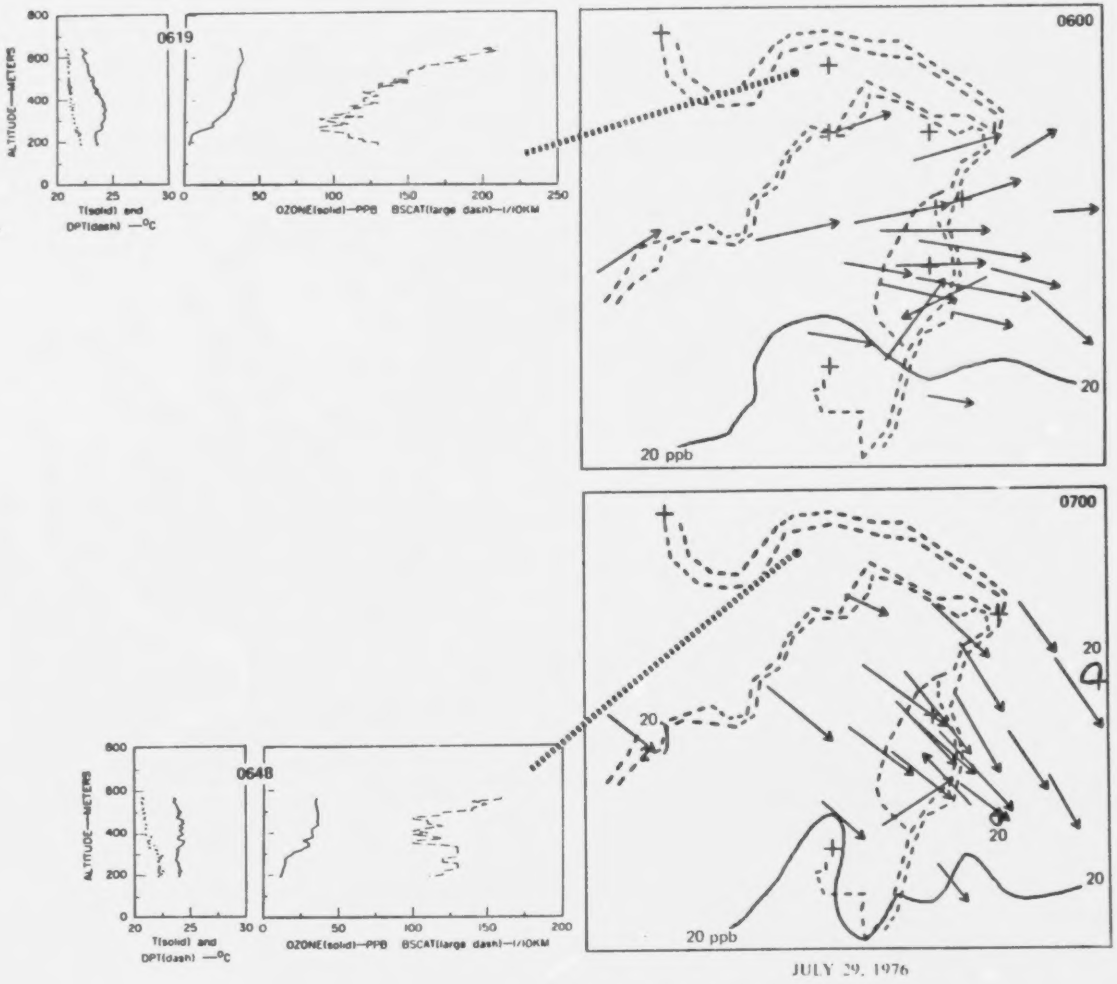


FIGURE 10 ST. LOUIS OZONE CONCENTRATIONS ON THE MORNING OF JULY 29, 1976

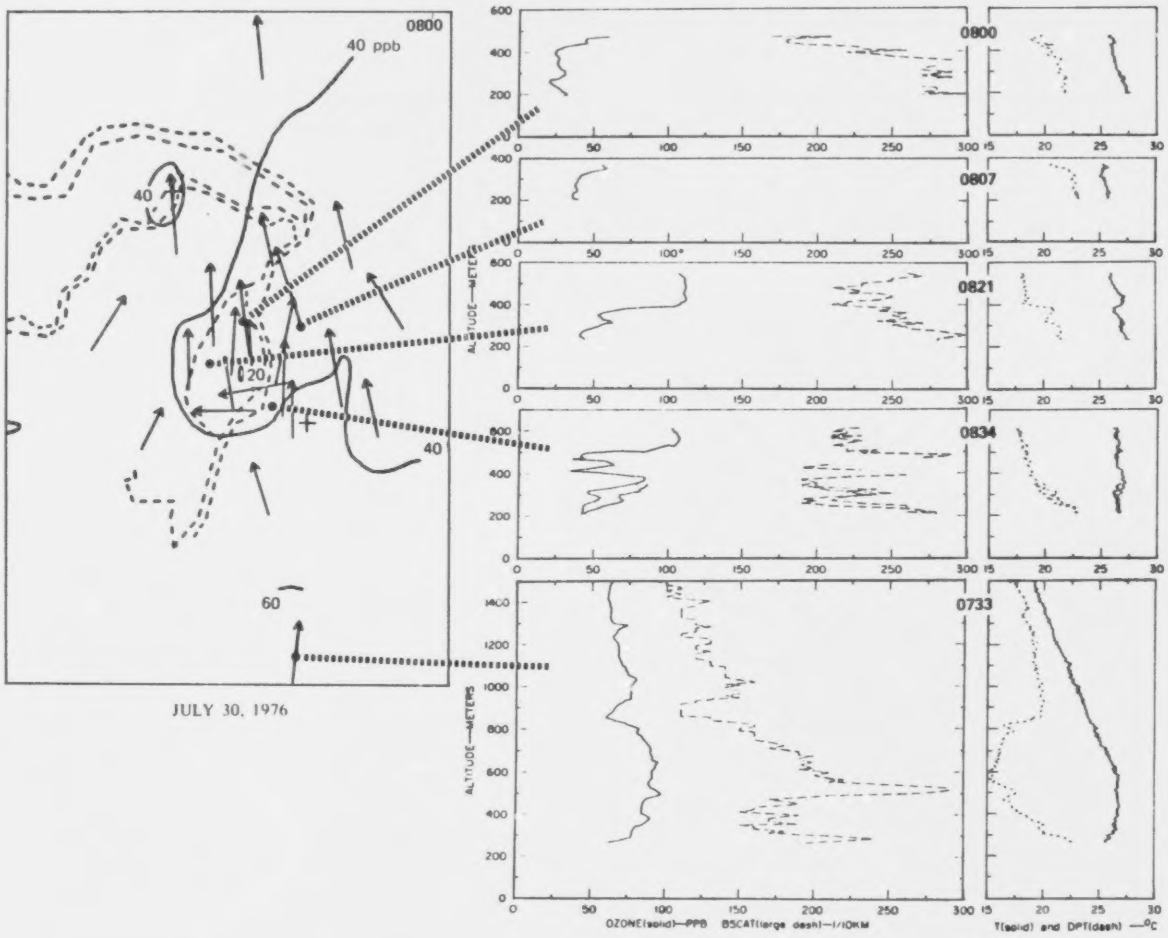


FIGURE 11 ST. LOUIS OZONE CONCENTRATIONS ON THE MORNING OF JULY 30, 1976

Generally, the air flow was light and from the south. At this time, St. Louis was located on the cold-air side of a weak stationary front, and in the southwest quadrant of a weak high-pressure area. The upper three profiles on the right side of the figure were taken at 0800, 0807, and 0821 CST. They show clearly the influence of the city. The observed surface concentrations of about 30 ppb are much less than the 60 to 110 ppb that was observed above the same sites. There is even evidence of the city's effects in the temperature profile. Apparently the surface roughness and added heat from the city prevented the formation of an inversion or isothermal layer at the surface, such as is evident in the profile taken ouside the city at 0834 CST and from the upwind station at 0733 CST. Both those stations show some evidence of lower concentrations at the surface, but in the case of the upwind station, the lower surface concentration is probably the result of the surface-based stable layer acting in combination with surface destruction in the manner described before. The nephelometer profile taken at 0834 CST shows some evidence of high aerosol concentrations at the surface, so the reduced ozone concentration might well have been caused by increased NO. This same pair of profiles also shows some evidence of a plume aloft, with reduced ozone and high nephelometer readings at around 400-500 m altitude.

Figure 12 shows conditions during the day of July 30, 1976. It is somewhat difficult to classify the two profiles taken inside the city at 0844 and 0925 CST, because of their limited extent. However, on the basis of profiles shown in Figure 11, it is presumed that ozone concentrations increased somewhat with height above the top of the profiles that are shown in Figure 12, so the later profiles have been classified as Type F. The profile taken at 0915 CST shows very uniform ozone concentration with height, with little evidence of influence from the NO emissions of the city, although it does appear to be downwind of the city, as evidenced by the high nephelometer reading in the lowest layer. The profile taken above Smartt Field at 0952 CST shows evidence of being reasonably constant, with height up to the top of the mixing layer at about 500 m; the other profiles taken on the same day at other locations suggest that the concentration is probably much the same above the mixing layer as within it, so this profile has been classified as Type A.

Figure 13 shows five profiles taken between 0830 and 0930 CST on the morning of August 4, 1976. All these profiles have rather limited vertical extent and so their classification is difficult. St. Louis was in the western part of a very large high-pressure area on this day, thus the light south-southeasterly winds shown in the figure. The profile taken over the city at 0856 CST was classified as a Type F, based on the surface level concentration derived from the analysis of ground-level ozone observations. It was not possible to classify the vertical profile taken over the city at 0913 CST because of its limited vertical extent. The upwind profile taken at 0831 CST was assumed to be a Type A, partly on the basis of its upwind location and partly because of the analysis of surface concentrations. The downwind profile taken at 0903 CST is probably a Type C profile, because of the higher concentrations observed at the surface. The remaining profile, taken at 0924 CST, was classified

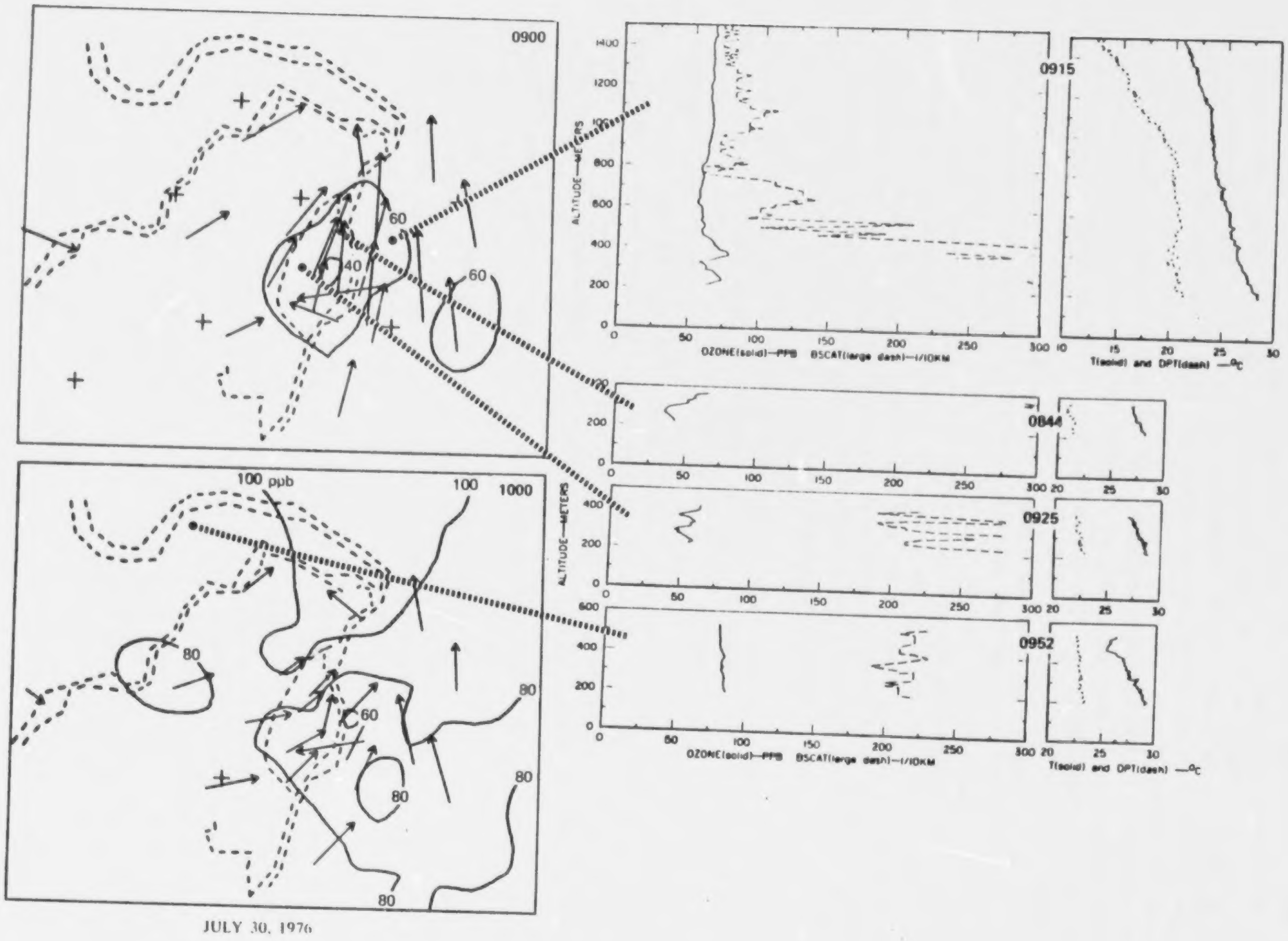
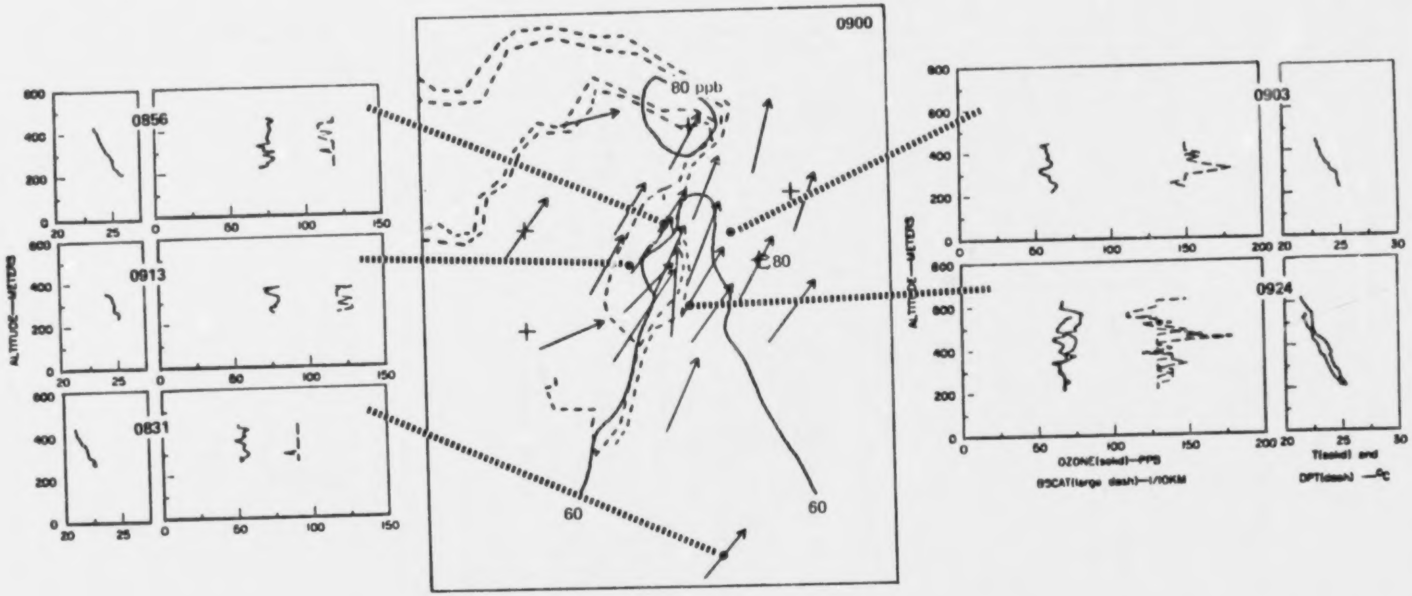


FIGURE 12 ST. LOUIS OZONE CONCENTRATIONS DURING MIDMORNING ON JULY 30, 1976



AUGUST 4, 1976

FIGURE 13 ST. LOUIS OZONE CONCENTRATIONS AT 0830 TO 0930 CST ON THE MORNING OF AUGUST 4, 1976

as Type D because of the uniformity of its concentration within the mixed layer. It was assumed that concentrations above the mixed layer were somewhat lower, more nearly like those observed at the upwind station. The depth of the mixed layer could not be determined from these vertical profiles, but it was available from analysis of lidar (laser radar) observations taken at site 141 (see Figure 6) and reported by Endlich et al. (1978).

Figure 14 shows five more vertical profiles taken later in the day on August 4, 1976. With the exception of the profile taken at Smartt Field, it appears that the ozone concentrations are reasonably uniform in the vertical from the surface upward, even within the city itself. This is probably because vertical mixing had been fairly vigorous and offset most of the NO or surface destruction. The profile taken at 1027 CST above Smartt Field shows reasonably uniform concentrations above the surface, but the much higher concentrations shown at the surface are likely incorrect and may reflect an artifact of the smoothing process used in the data analysis (see Endlich and Mancuso, 1968; Mancuso and Endlich, 1973). In classifying this profile as Type D, we have assumed that the surface concentration is about 70 to 80 ppb.

Figure 15 shows two profiles measured on the morning of August 12, 1976. St. Louis was in the western part of a high-pressure area at this time, but showers had been observed to the west at Kansas City and to the north at Springfield, Illinois during the morning. That shower activity may have been associated with the squall line shown over the Great Lakes on the National Weather Service analysis. Such a trough or squall line may have caused the wind shift shown in the figure. In any event, it appears that there was substantial vertical mixing. That strong vertical mixing would normally be associated with nearly uniform vertical distribution of ozone. If the analysis of surface ozone concentrations is correct, then there was probably a stable layer near the surface at the time of the earlier profile (0629 CST). The rather low concentrations at the surface are characteristic of a Type B profile. Above the lowest layers, concentrations were nearly uniform except for the pronounced depression in ozone concentration at around 500 m. That depression was probably caused by emissions from a power plant. By 0841 CST, the profile was nearly uniform with height, ranging from about 75 ppb at the surface down to about 55 ppb at low altitudes, but staying generally between 70 and 80 ppb at higher altitudes. The 0900 CST analysis indicates that ozone production had begun downwind of St. Louis by that hour.

2. Los Angeles

a. Background

Table 3 summarizes the vertical profile data available from the Los Angeles Basin. The profiles measured before September of 1973 are based on the work of Blumenthal et al. (1974). The profiles for the later

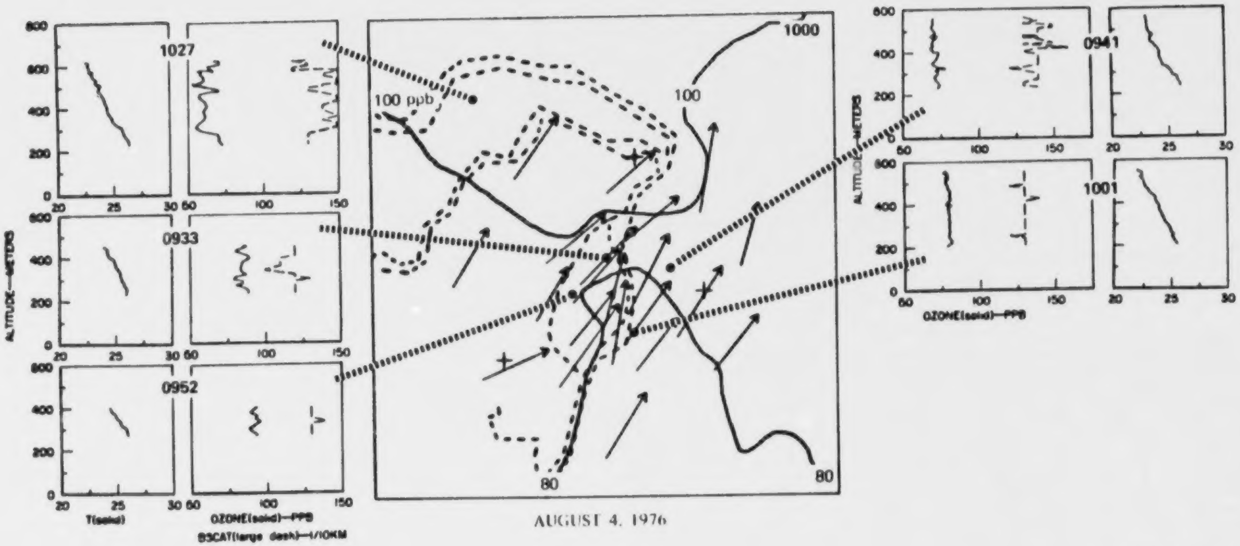


FIGURE 14 ST. LOUIS OZONE CONCENTRATIONS AT 0930 TO 1030 CST ON THE MORNING OF AUGUST 4 1976

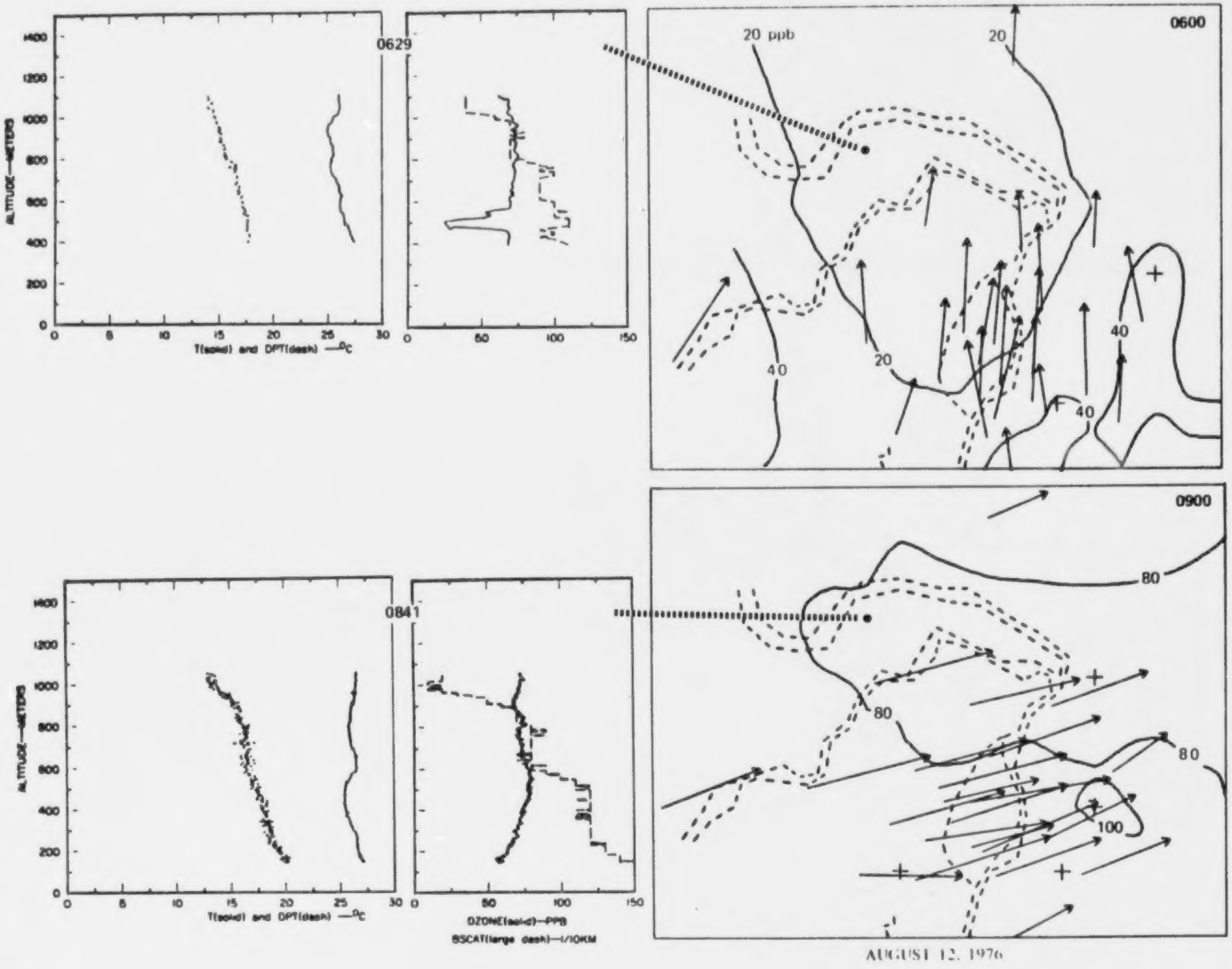


FIGURE 15 ST. LOUIS OZONE CONCENTRATIONS DURING THE MORNING OF AUGUST 12, 1976

Table 3

SUMMARY OF OZONE PROFILES STUDIED FROM THE LOS ANGELES BASIN

Date	Time (PST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 16)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
720921	1220	2.0				Redlands		x			A	70	70
	1252	0.3				Long Beach		x			D	170	160
	1525	1.3				Brackett		x			F	140	120
	1636	2.0		3	290	Redlands		x			A	140	140
721018	0920	0.5	D			Shepherd		x			B	0	20
	1257	0.7	D			Shepherd		x			A	5	10
730719	1638	0.8				Rialto		x			D	300	300
730725	1306	0.2						x			F	130	150
	1327	0.5		5	190	Hawthorne		x			D	390	400
	1555	0.4		7	190	Shepherd		x			F	180	210
	1607	0.8		7	250	El Monte		x			D	320	350
	1624	0.4		8	250	Brackett			x		D	210	210
	1705	0.9		7	280	Corona		x			C	320	250
730726	0725	0.7				Brackett		x			F	10	50
	1538	0.5				Rialto		x			D	140	140
	2139	0.5				Riverside		x			B	0	50
730727	0022	0.6				Riverside		x			B	0	60
	0400	0.8				Riverside		x			B	0	0
730816	1217	1.3		3.5	230	Redlands		x			D	230	240
	1237	1.1		3.5	230	Rialto		x			D	240	230
	1600	1.1				Redlands		x			D	320	340
730824	1100	1.0				Upland		x			F	160	160
	1221	1.3		4	250	Rialto		x			F	180	190

Table 3 (Concluded)

Date	Time (PST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 16)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
730919	1320	0.6	C	4	180	Pasadena		x			D	200	
	1336	0.5	C	4	200	El Monte		x			D	125	160
	1413	0.8	C	4	200	El Monte		x			D	175	200
	1452	1.2	D	6	200	Ontario			x		D	175	
	1554	1.0	D	4	260	Compton		x			F	40	100
730924	1521	1.0	D	5	210	Compton		x			A	25	25
731004	1325	0.6				Glendale		x			E	150	300
731005	1551	0.8	D	6	190	El Monte		x			F	50	
	1630	0.8	D	7	240	Upland			x		D	175	190
731025	1415	0.6	D	5	140	Glendale		x			D	120	150
731028	1600	1.4				Mira Loma			x		D	200	210
731029	1412	0.7	C	3	200	Arcadia		x			E	140	180
731030	1431	0.6	C	3	160	Arcadia		x			D	120	145
731031	1231	0.8	C	4	230	San Marino		x			D	80	100
731107	1247	0.8	C	3	180	Santa Fe Basin		x			E	80	140
	1319	0.9	C	3	180	Arcadia		x			E	110	180
	1435	0.9	C	4	230	Cucamonga		x			E	170	200

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

dates come from the Los Angeles Reactive Pollutant Program (LARPP) and were taken from a report by Johnson and Singh (1977). This latter group was examined in somewhat more detail than the earlier profiles. For the earlier profiles, only that information which could be deduced from Blumenthal et al. (1974) is included in Table 3. Figure 16 shows key locations in the Los Angeles Basin.

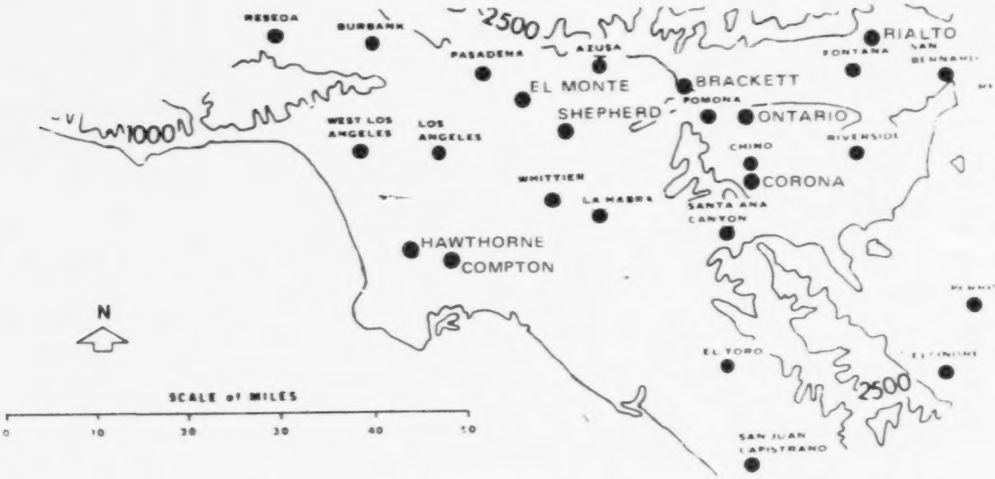


FIGURE 16 MAP OF SOUTHERN CALIFORNIA

Examination of Table 3 shows that most of the vertical profile measurements made in the Los Angeles Basin were made during afternoon hours. In fact, 35 of the 40 profiles were measured between noon and 1700 Pacific Standard Time (PST). Another bias in the data is caused by the extremely large urbanized area within the Los Angeles Basin. Virtually all the profiles must be considered as having been measured above the city. To a large extent, the Los Angeles profiles complement those from St. Louis by providing more afternoon coverage and more illustrations of the effects of urban emissions on the lower portions of an ozone profile.

Los Angeles also has some unique characteristics that cannot be generalized to other areas. For example, it was noted earlier that the persistent summertime subsidence inversion, in combination with the mountains surrounding the basin, sometimes produces ozone profiles of Type F by a mechanism different than that prevalent in other parts of the country. We discussed earlier Edinger's (1973) suggested mechanism for the injection of ozone into stable layers aloft. The July 19, 1973, observation of Blumenthal et al. (1974) at Rialto (shown in Figure 17) illustrates injection of ozone into the elevated inversion layer by upslope flow along the heated mountain slopes. Some of the examples from the LARPP study that are presented on later pages also seem to show the effect.

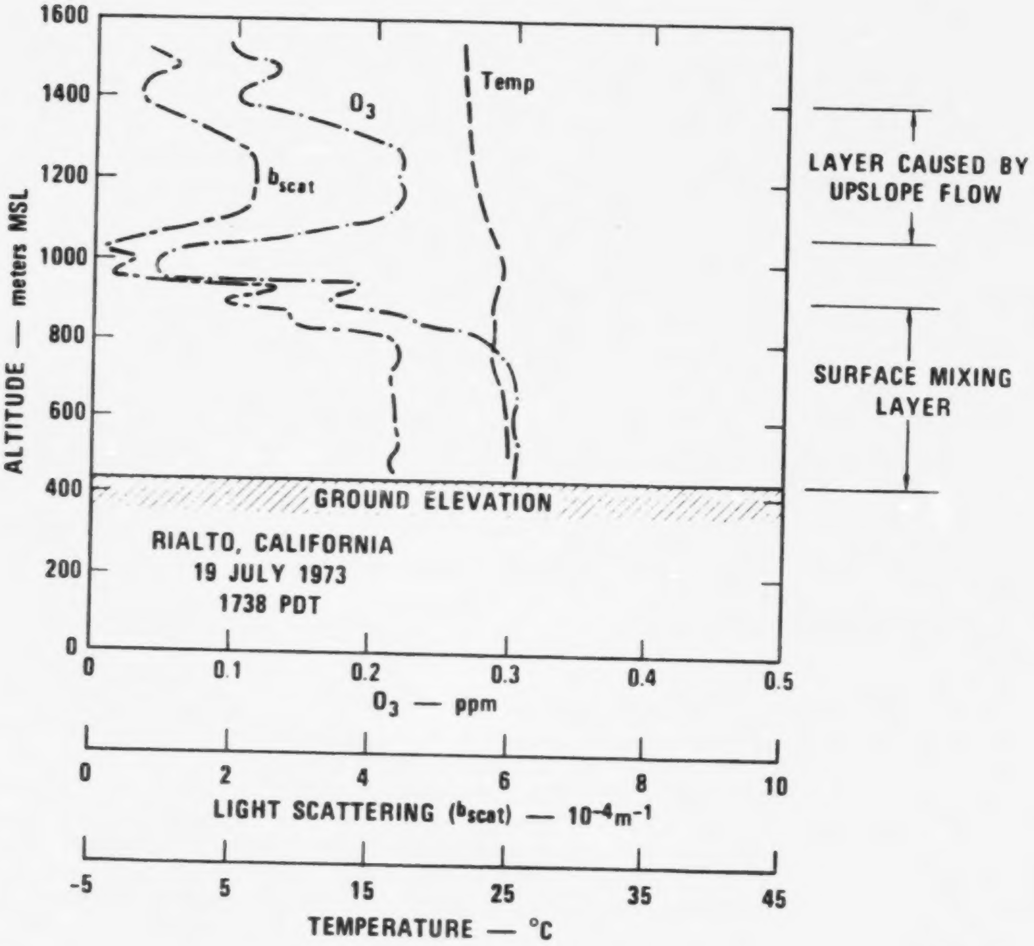


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FIGURE 17 EXAMPLE OF OZONE LAYER ALOFT, PROBABLY CAUSED BY UPSLOPE FLOW

b. Examples

Figures 18 through 22 show vertical ozone profiles that were measured on September 19, 1973, in various parts of the Los Angeles Basin. Vertical profiles of nephelometer readings (B_{scat}), nonmethane hydrocarbons (NMHC), and oxides of nitrogen (NO_x) are also shown. The temperature and dew point instruments were not functioning on this day. The locations where the profiles were measured are marked on the maps by circled stars. Surface wind observations and surface ozone concentrations are also shown on the maps, as they were for the St. Louis data. However, the plotting and analysis of the Los Angeles data were done by hand, rather than with an objective, computerized system, as was used for the St. Louis analyses.

The vertical profiles collected during the LARPP study were frequently interrupted at various altitudes by short intervals when the helicopter flew a rectangular pattern at constant altitude. All the data collected during one of these rectangular segments were averaged and plotted on the profile. The horizontal bars show the standard error of those observations. The large standard errors resulted primarily from the fact that the data collection system was subject to considerable interference, and there were frequent "noise spikes" that caused scatter in the data points. Usually it is quite easy to identify the errant points visually and to ignore them in the interpretation of the profiles.

Figure 18 shows the ozone profile measured at about 1307 to 1320 PST above Pasadena on September 19, 1973. The bottom of the profile corresponds with the approximate top of the mixing layer, so that it is not possible to classify the profile with absolute certainty. Profiles collected elsewhere during the afternoon showed rapid decreases in pollution concentrations with height at the approximate top of the mixing layer. This suggests that the 200 ppb (20 pphm) surface concentrations probably extended throughout the depth of the mixing layer. At about 1300 m there was a peak in ozone concentration, and also in the backscatter and NO_x profiles which suggests upslope injection of pollutants into the stable layer aloft.

Figure 19 shows the vertical profiles over El Monte somewhat later on the same day. The ozone profile shown in Figure 19 is a good example of the Type D profile and lends further support to classifying the profile in Figure 18 as Type D. The profile in Figure 20 has also been classified as Type D, although there is considerable scatter in the data points. We assumed that there was little change in the characteristics of the profile during the 1/2-hour that elapsed between the measurements shown in Figure 19 and those shown in Figure 20.

Figure 21 shows the ozone profile measured over the Compton area between about 1523 and 1554 PST. This profile has been classified as Type F. The mechanism producing this profile is not entirely clear, but it appears that there is considerable ozone aloft within the stable

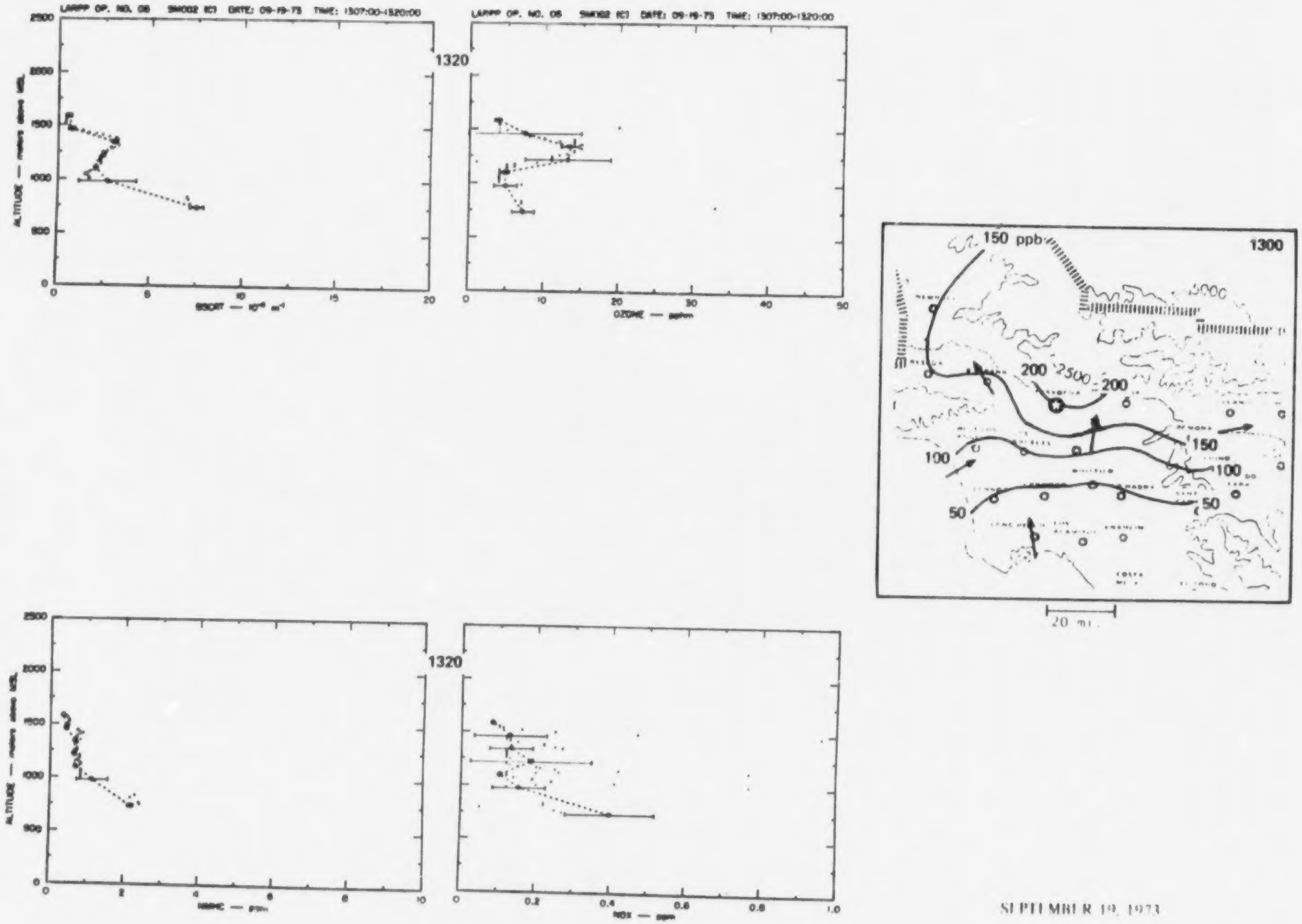

FIGURE 18 PASADENA PROFILES DURING THE AFTERNOON OF SEPTEMBER 19, 1973

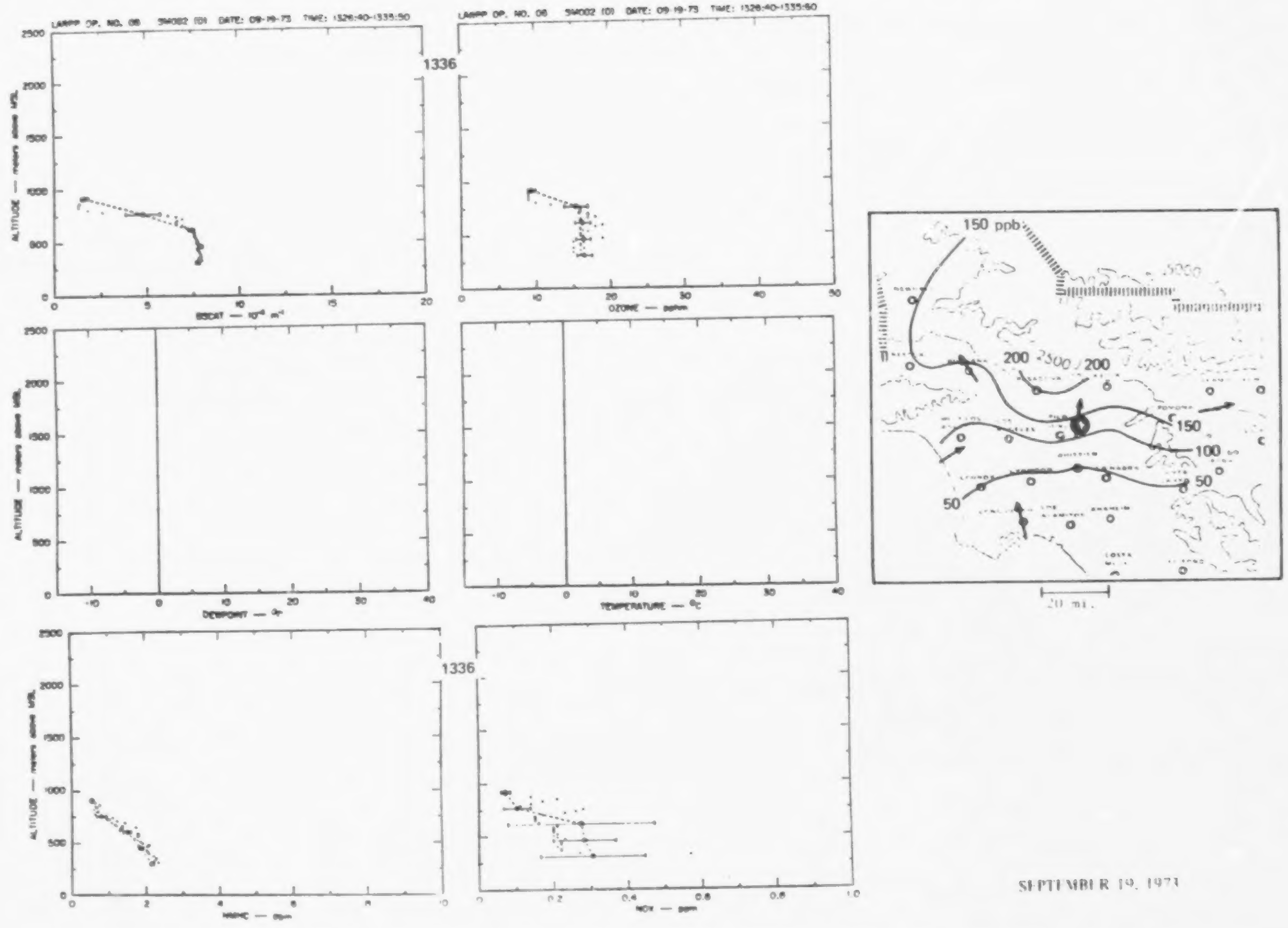

FIGURE 19 EL MONTE PROFILES DURING THE AFTERNOON (1336 PST) OF SEPTEMBER 19, 1973

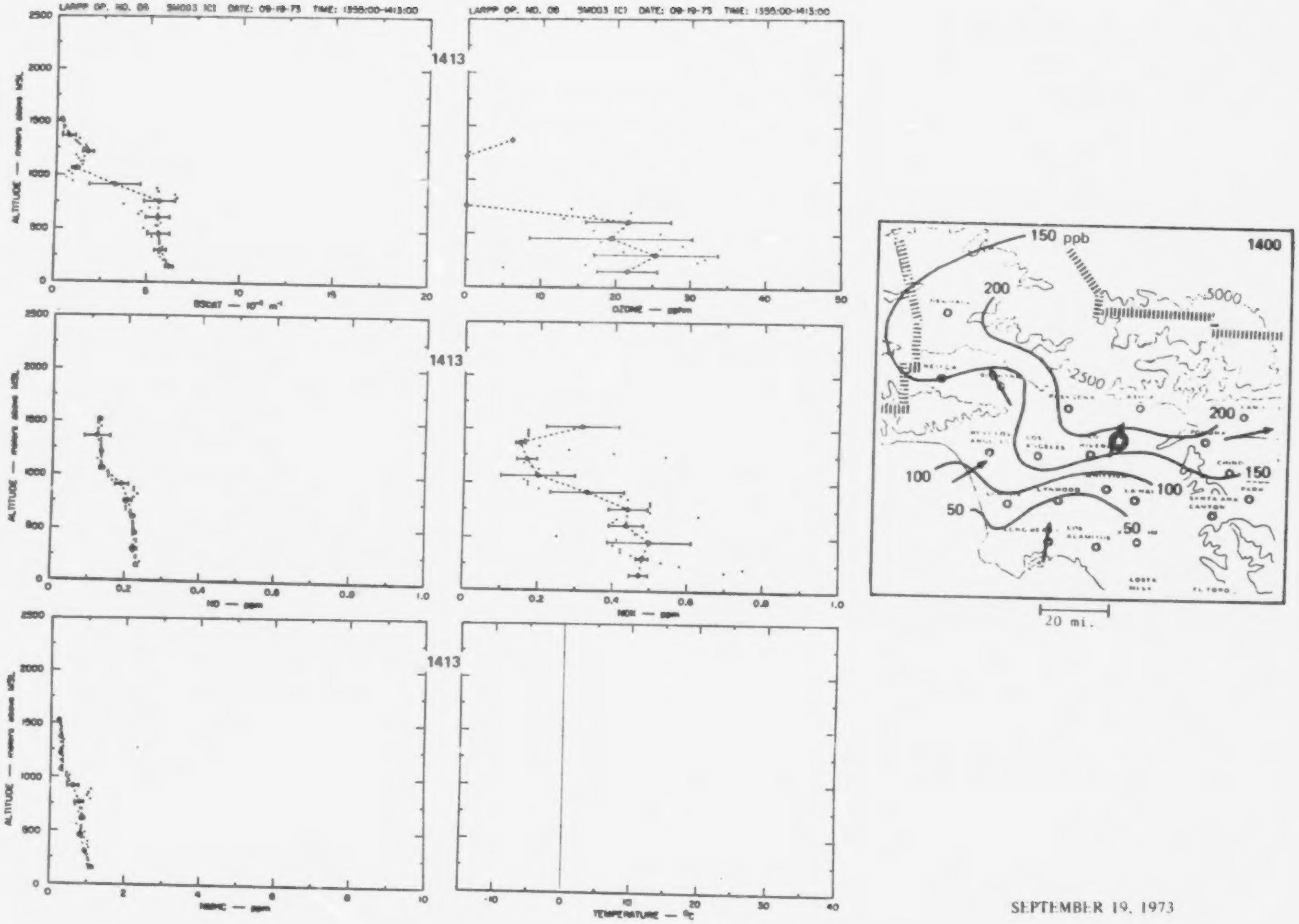

FIGURE 20 EL MONTE PROFILES DURING THE AFTERNOON (1413 PST) OF SEPTEMBER 19, 1973

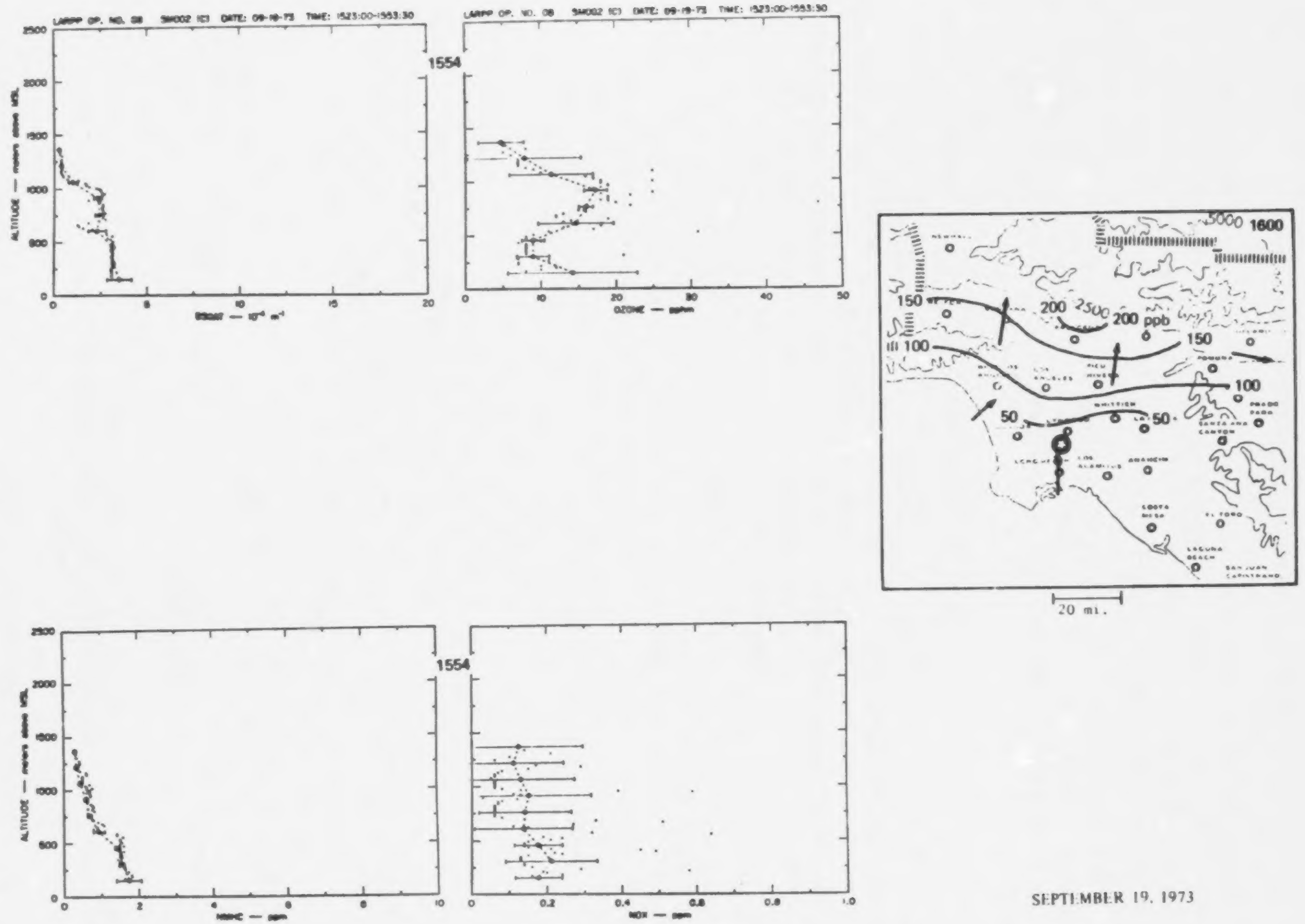

FIGURE 21 COMPTON PROFILES DURING THE AFTERNOON OF SEPTEMBER 19, 1973

layer and that this ozone aloft is being undercut by clean marine air flowing onshore with the sea breeze. The wind arrows (shown in the figure) give clear evidence of a well established sea breeze.

Figure 22 shows the conditions above Compton on the afternoon of September 24, 1973. Unlike the case shown for the same location in Figure 21, the low concentrations observed at the surface were found to extend upward through the top of the marine layer (at about 1000 m as shown by the temperature and dew point traces) and well into the stable layer. The nephelometer readings show a marked decrease at the top of the mixing layer, but this may simply reflect the change in humidity, causing particles to dry out and become smaller, less effective light scatterers.

Figure 23 shows the ozone profiles measured above El Monte on the afternoon of October 5, 1973. Figure 24 shows conditions above Upland, somewhat farther to the east, later during the same day. No data are available below about 800 m above El Monte. Very dry conditions (indicated by the negative dew point temperatures) suggest that all the data were collected above the marine layer. The ozone concentrations within the inversion layer, above the marine layer, were about 100 ppb (10 pphm) or greater. At the surface, the concentrations were about 50 ppb. The high concentrations of ozone trapped within the inversion layer and the lower concentrations below provide reason for classifying this profile as Type F. The Upland temperature and dew point profiles shown in Figure 24 confirm that the top of the mixed layer was below 800 m. It has been assumed that the relatively high ozone concentrations shown in the lower parts of the profiles extend to ground level; this is based on an extrapolation of the isopleth analysis shown in the figure. Based on this assumption, the profile was classified as Type D, but this is admittedly uncertain.

Figure 25 shows conditions on October 25, 1973, above Glendale. The demarcation between the relatively polluted marine layer below about 600 m and the cleaner, drier air above that height was quite pronounced. The NO_x and nephelometer (Bscat) readings dropped to near zero values above the stable layer. Ozone concentrations also dropped abruptly at the top of the mixed layer, in the manner of a Type D profile.

Figure 26 shows the conditions in the eastern parts of the Los Angeles Basin on the afternoon of October 28, 1973. The mixing layer appears to have been fairly deep, about 1300 m judging by the nephelometer readings. Very high concentrations of ozone had built up within the mixing layer as the air moved over the basin and beyond the most heavily urbanized areas. Concentrations of 200 ppb or greater were found throughout the mixing layer. This relatively uniform distribution of ozone within the mixing layer, and the abrupt decrease at the top, is characteristic of a Type D profile.

Figure 27 shows the conditions during the afternoon of the next day, October 29, 1973, above Arcadia. Although there are no temperature

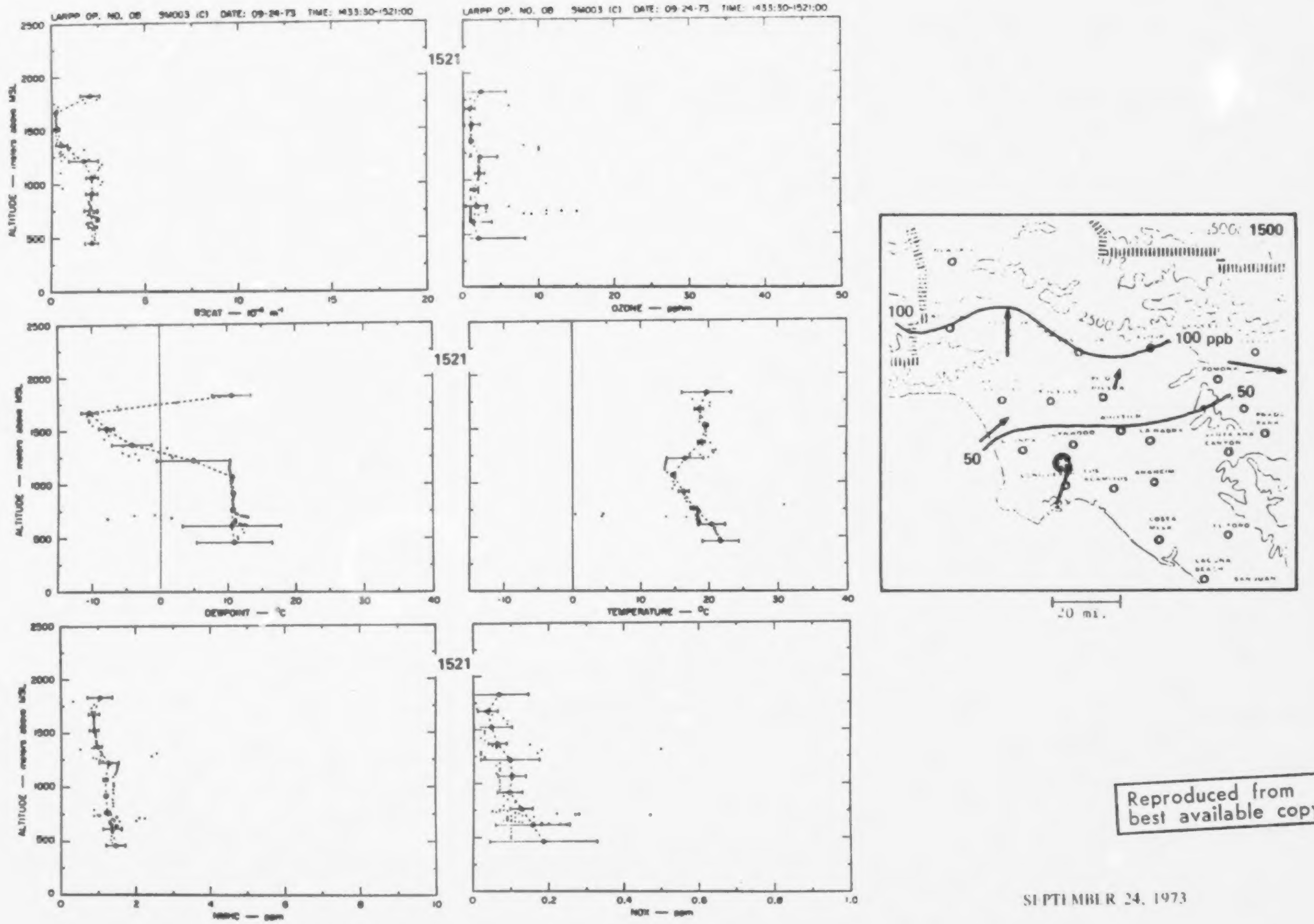

FIGURE 22 COMPTON PROFILES DURING THE AFTERNOON OF SEPTEMBER 24, 1973

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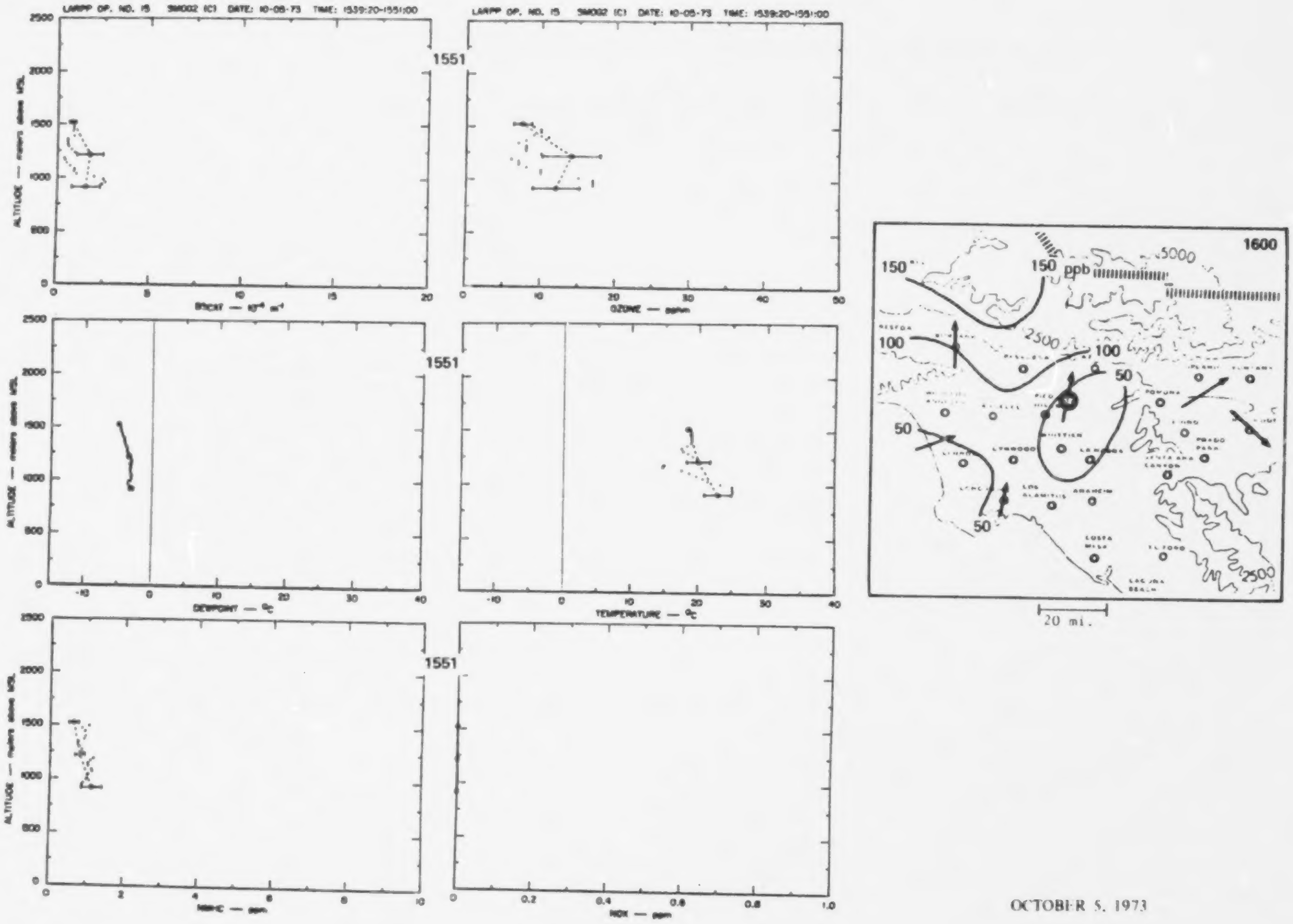
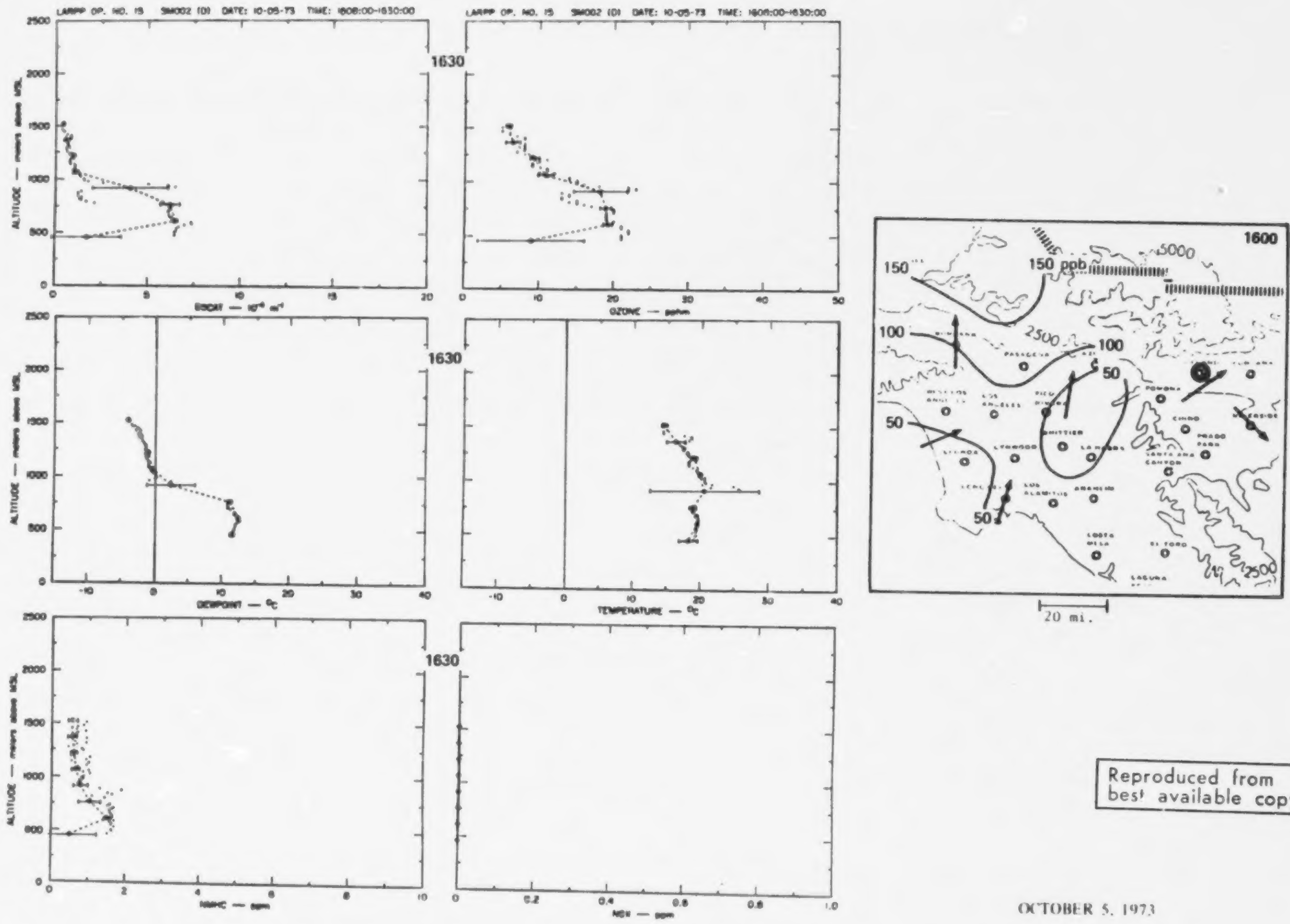


FIGURE 23 EL MONTE PROFILES DURING THE AFTERNOON OF OCTOBER 5, 1973



OCTOBER 5, 1973

FIGURE 24 UPLAND PROFILES DURING THE AFTERNOON OF OCTOBER 5, 1973

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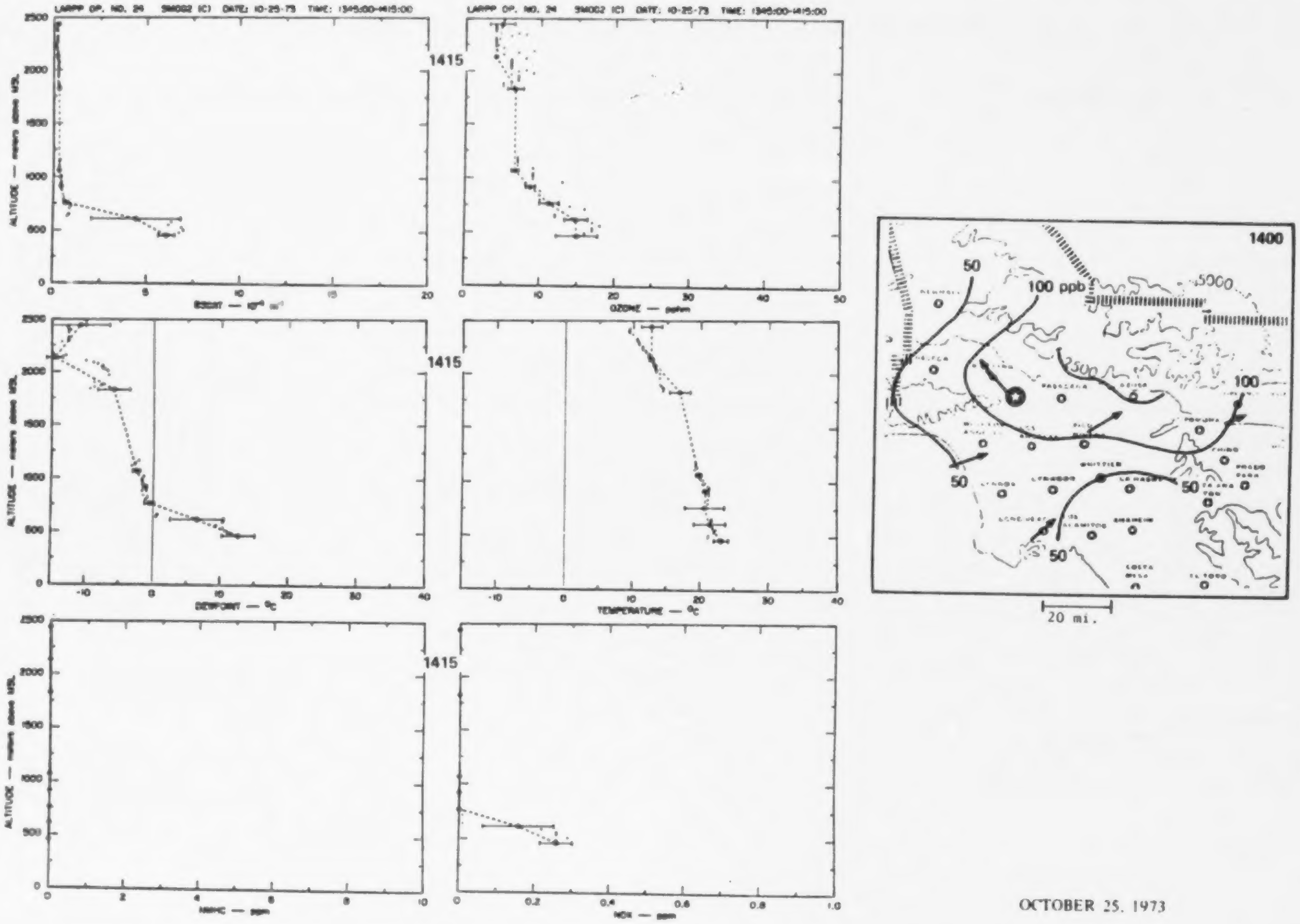
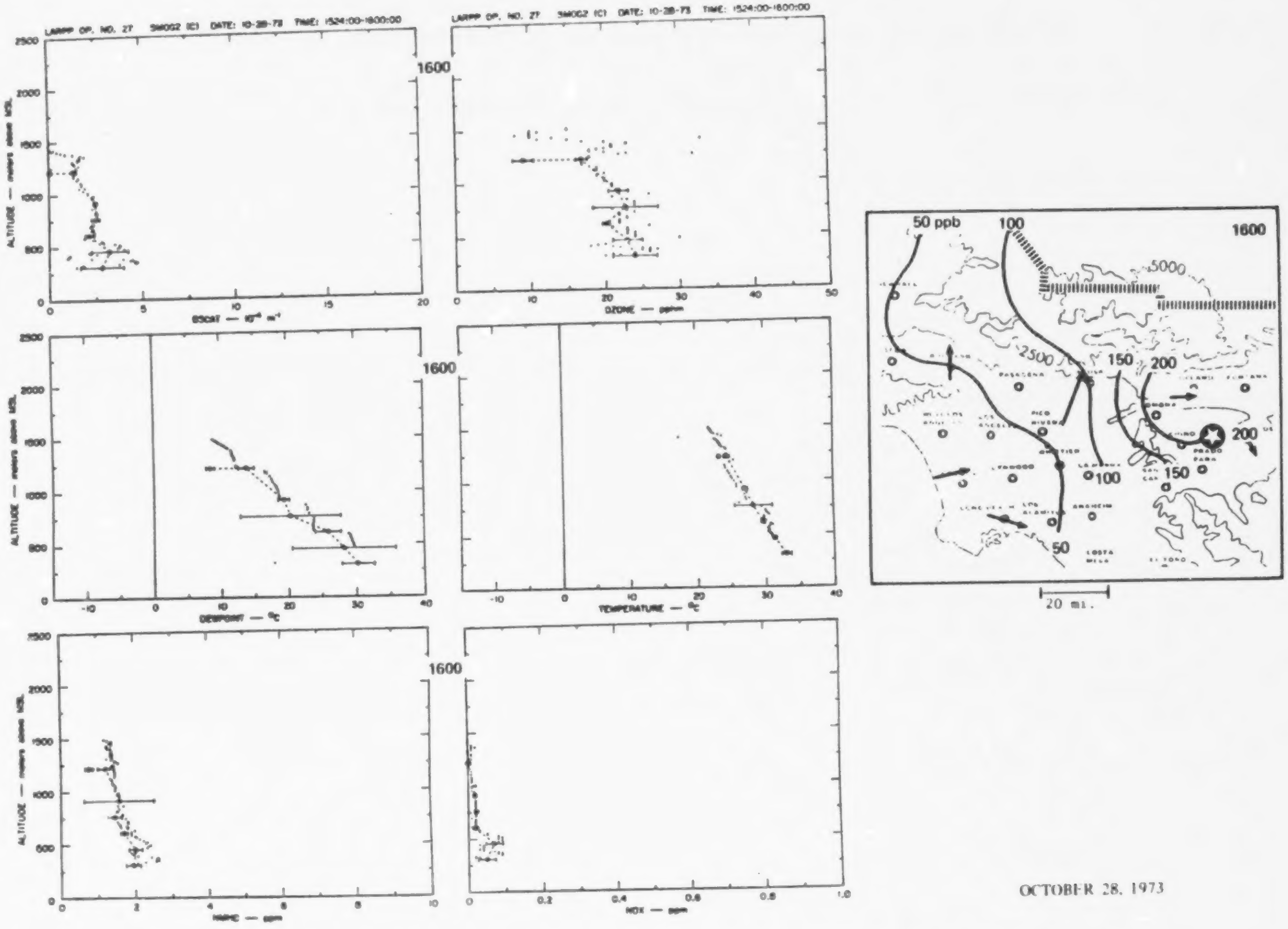


FIGURE 25 GLENDALE PROFILES DURING THE AFTERNOON OF OCTOBER 25, 1973



OCTOBER 28, 1973

FIGURE 26 MIRA LOMA PROFILES DURING THE AFTERNOON OF OCTOBER 28, 1973

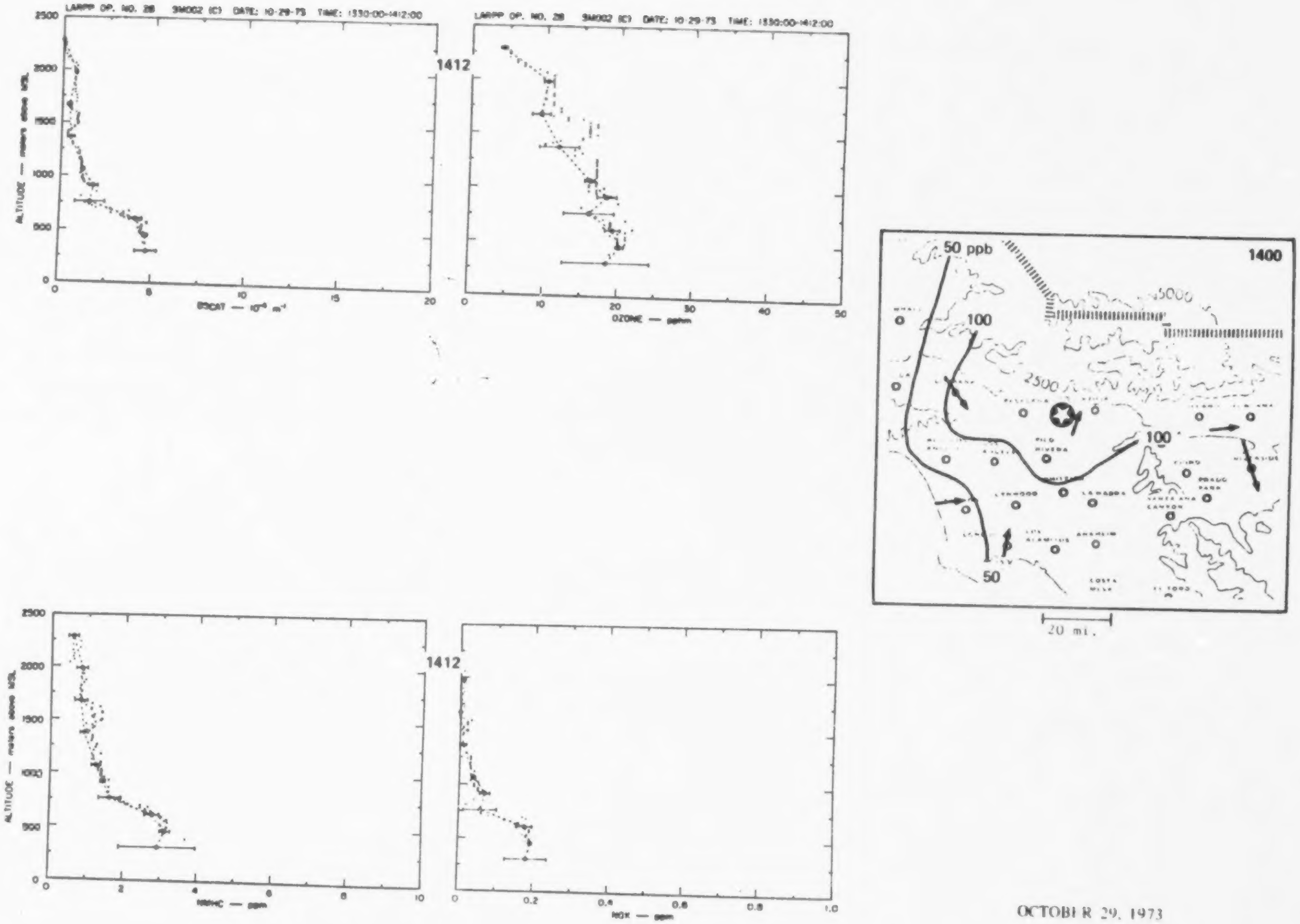


FIGURE 27 ARCADIA PROFILES DURING THE AFTERNOON OF OCTOBER 29, 1973

or dew point measurements available to define the location of the inversion, it appears from the NMHC, NO_x and nephelometer (Bscat) profiles that the top of the polluted layer was at about 600 m. Ozone concentrations within the upper part of this layer were near 200 ppb, although at the surface they were less than 150 ppb. The fact that the ozone concentrations do not decrease rapidly with height at the top of the mixing layer may indicate the presence of ozone trapped in the stable layer above this foothill location.

Figure 28 shows conditions above Arcadia on the afternoon of October 30, 1973. Although the dew point profiles suggest that the top of the marine layer might be at 600 m, all the other traces shown in the figure indicate a deeper mixing layer, with the top at about 1000 m. It appears that the mixing is vigorous enough to have offset most of the effects of destruction near the surface. The surface concentrations are around 120 ppb. Those at higher altitudes are about 140 to 150 ppb.

As is shown in Figure 29, ozone concentrations above San Marino during the afternoon of October 31, 1973, were fairly uniform up to a height of 1400 m where they dropped from about 100 ppb to 50 ppb. Concentrations at the surface were around 80 ppb. There is some evidence in the NO_x and NMHC profiles that the top of the polluted layer is at about 900 m rather than 1400 m. The ozone profile gives some evidence of this also, but there appears to have been an influx of higher ozone concentrations aloft. The dew point profile shows a corresponding, slightly moist, layer at about the same height as the increased ozone concentrations. The lower portions of the ozone profiles shown in Figure 29 are typical of the Type D profile, while the upper portions are like the Type F profile that arises from Edinger'S (1973) hypothesized mechanism, which introduces ozone into a stable layer aloft.

Figures 30 through 32 show conditions over three different locations in the Los Angeles Basin during the early afternoon of November 7, 1973. In all three examples, the ozone profiles have been classified as Type E, because the vertical mixing has not been sufficient to compensate for the destruction at the surface. Although fairly vigorous mixing is indicated, it appears that the destructive processes were sufficient to reduce the ozone concentrations in the lower layers by 100 ppb or more below the concentrations observed at higher altitudes. For example, Figure 30 shows that while concentrations aloft were 180 ppb or more, surface concentrations were about 80 ppb in this area. Figure 31 shows that concentrations above Arcadia were generally greater than 200 ppb within the mixing layer, but at the surface they were only about 100 ppb. For the example shown in Figure 32, surface concentrations were around 150 ppb, while aloft over Cucamonga, the concentrations exceeded 250 ppb.

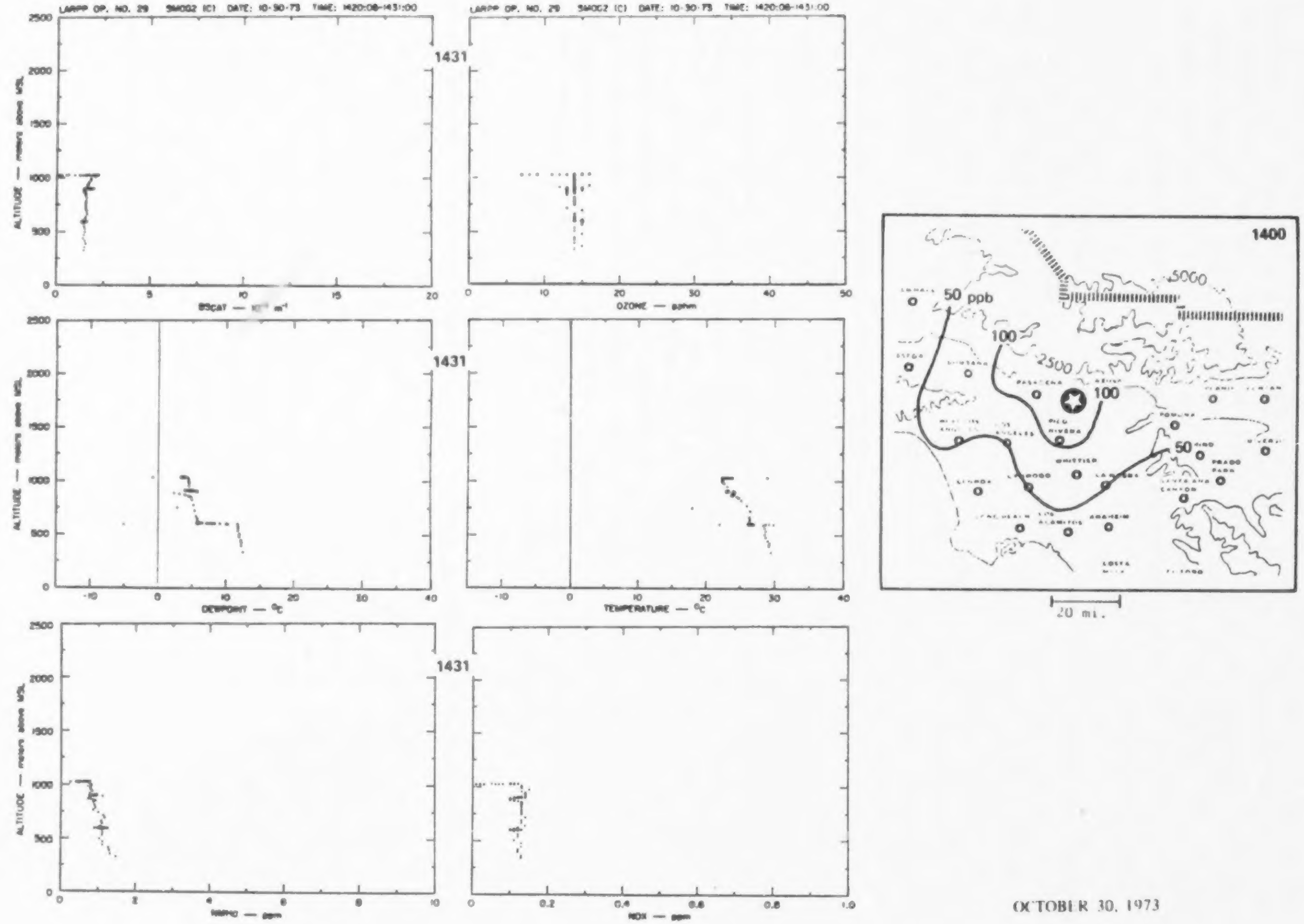


FIGURE 28 ARCADIA PROFILES DURING THE AFTERNOON OF OCTOBER 30, 1973

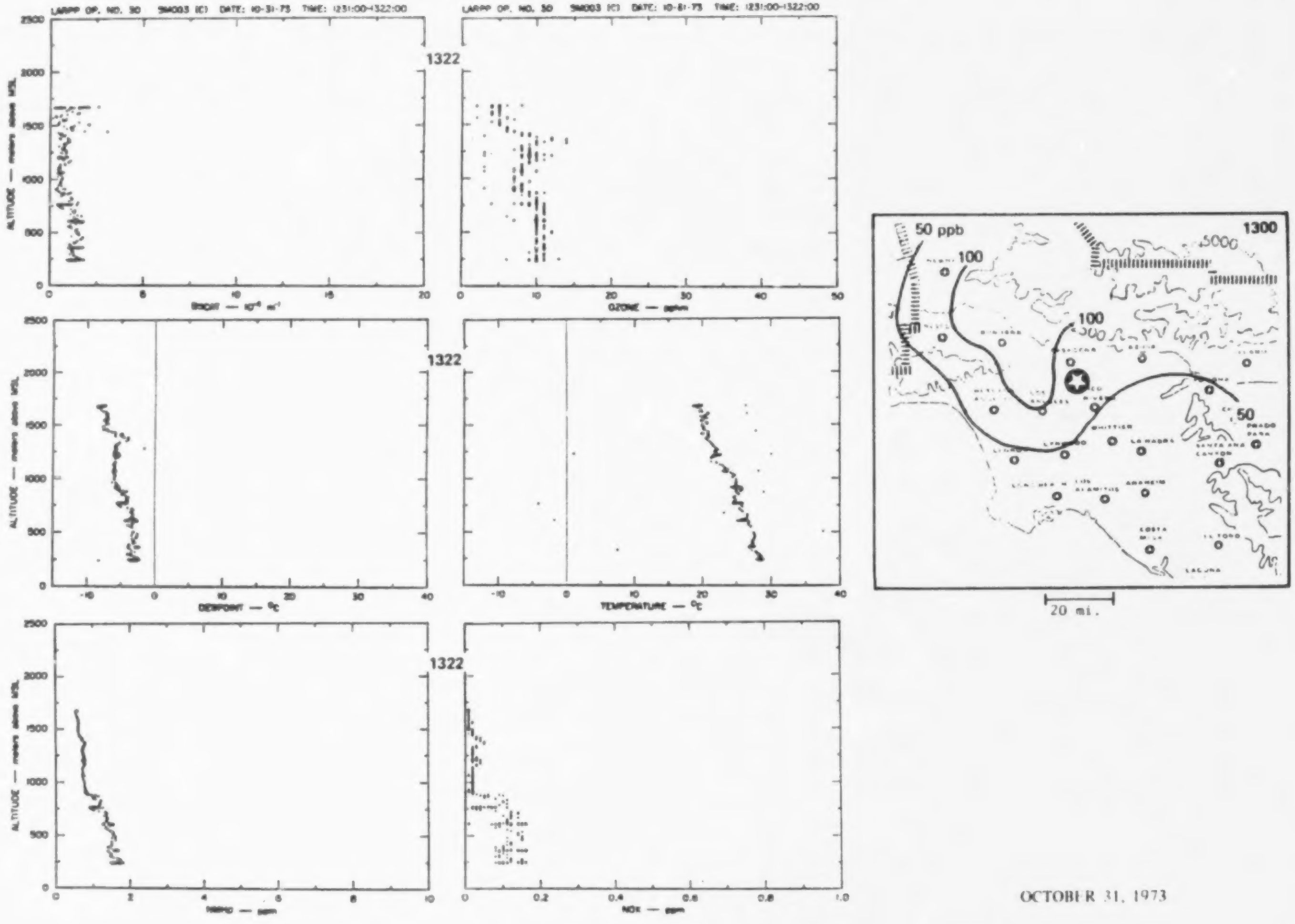
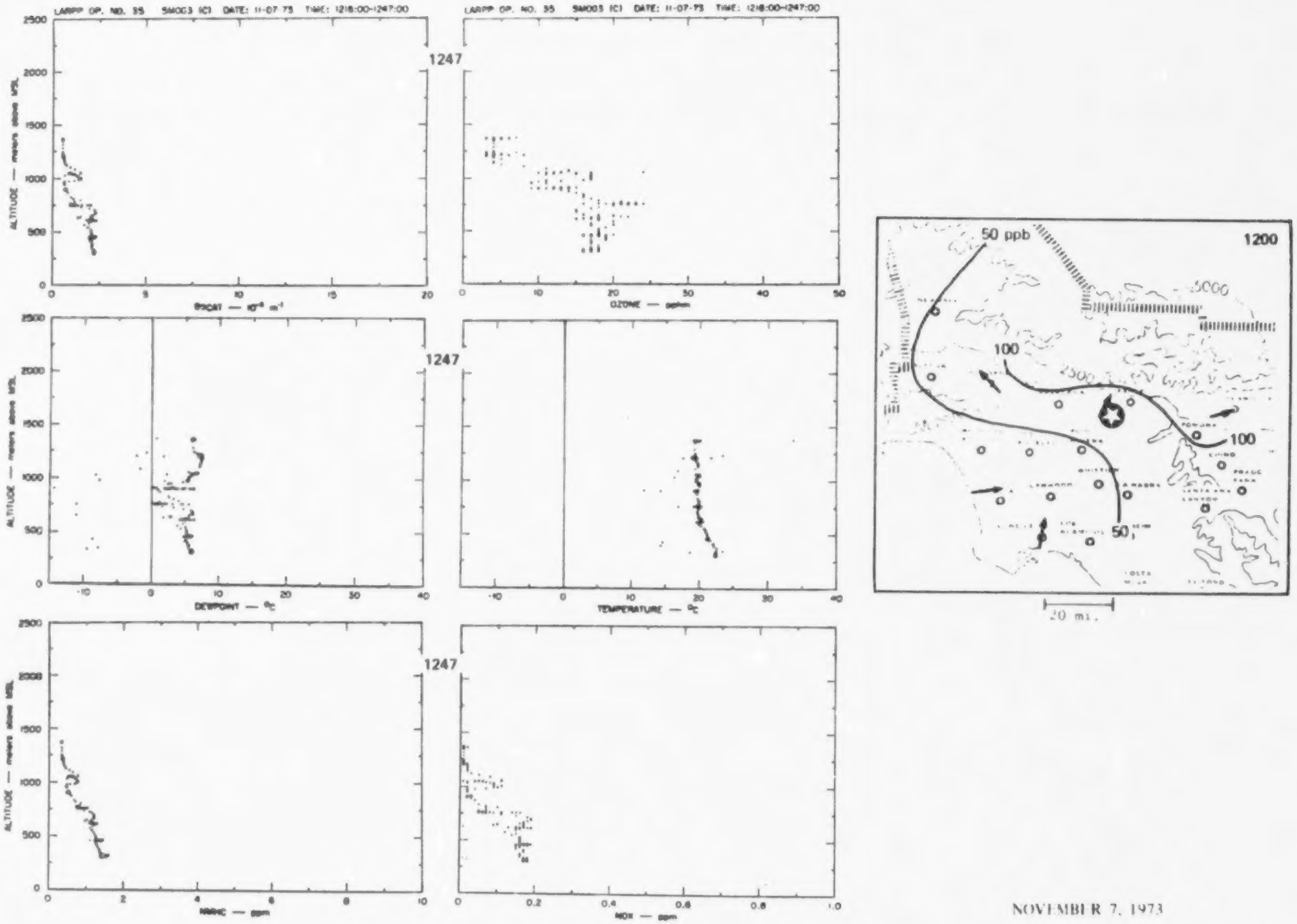


FIGURE 29 SAN MARINO PROFILES DURING THE AFTERNOON OF OCTOBER 31, 1973



NOVEMBER 7, 1973

FIGURE 30 PROFILES OVER THE SANTA FE FLOOD CONTROL BASIN DURING THE AFTERNOON OF NOVEMBER 7, 1973

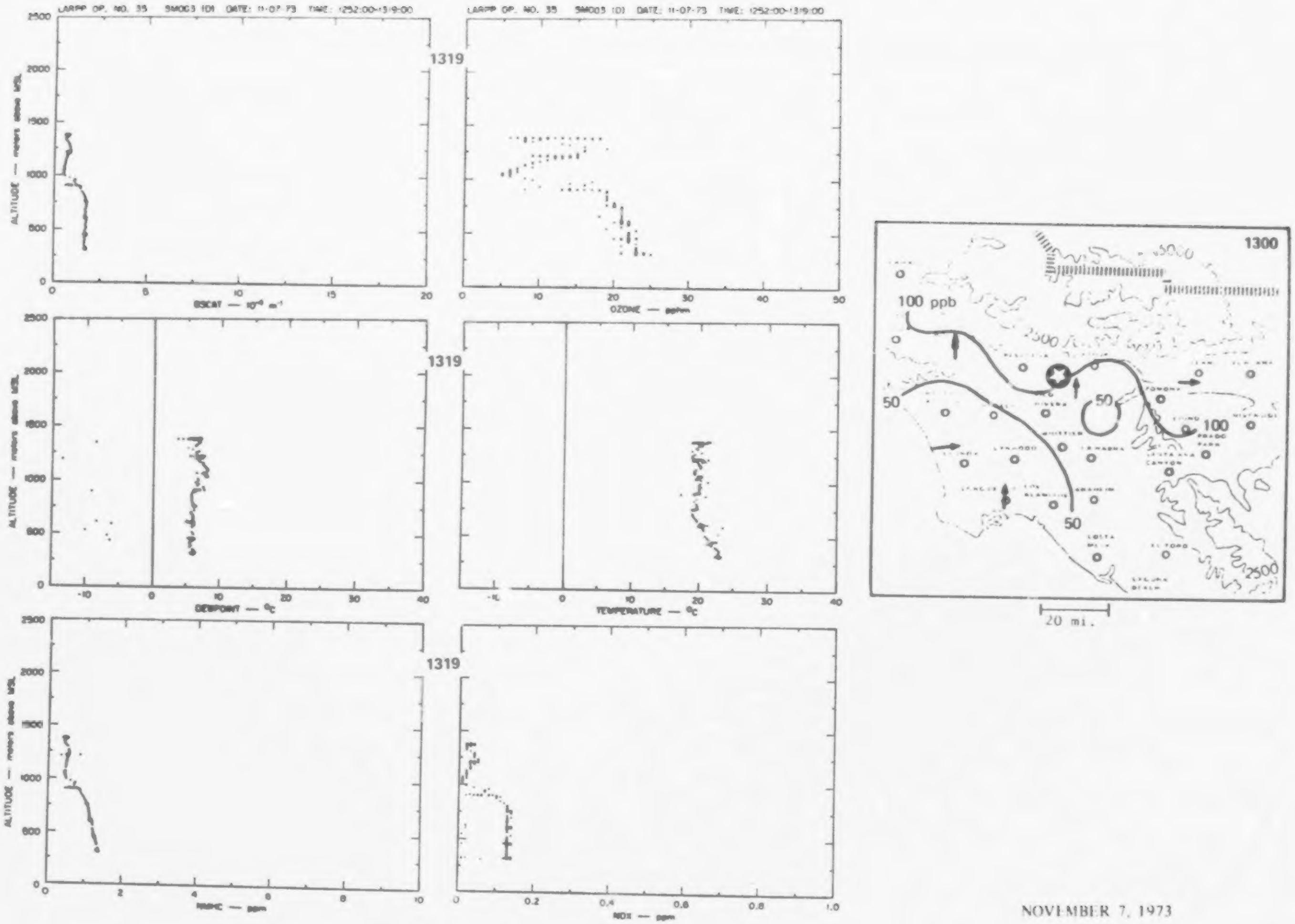
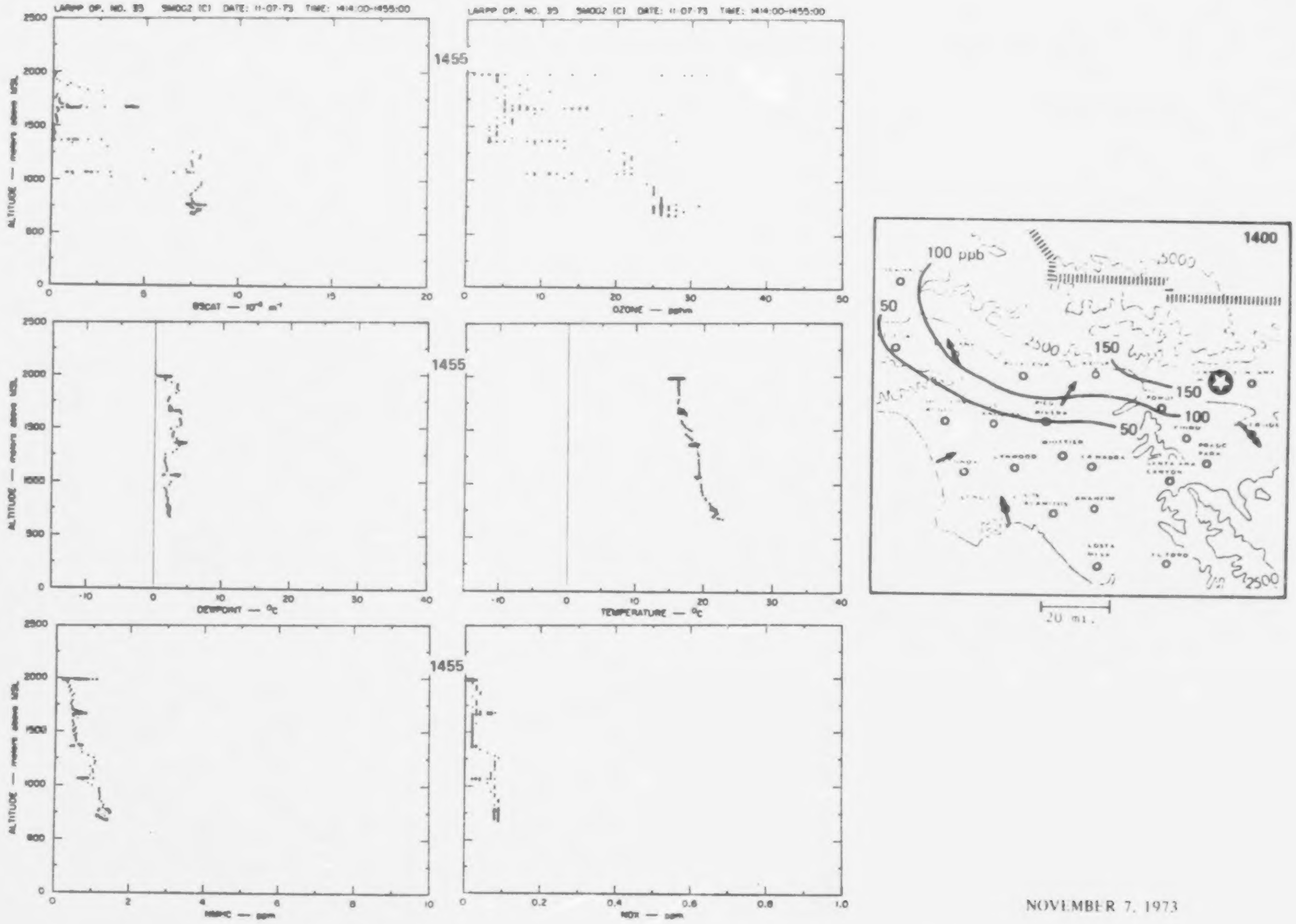


FIGURE 31 ARCADIA PROFILES DURING THE AFTERNOON OF NOVEMBER 7, 1973



NOVEMBER 7, 1973

FIGURE 32 CUCAMONGA PROFILES DURING THE AFTERNOON OF NOVEMBER 7, 1973

3. Houston

a. Background

Table 4 summarizes the 30 profiles examined from the Houston area. All the vertical profile information and much of the meteorological information were obtained from the report of Westberg et al. (1977). The measurements of surface ozone concentrations were obtained from the data archived as part of the Houston Area Oxidant Study (HAOS; see, e.g., Ludwig, Martinez, and Nitz, 1978). Morning and afternoon hours are reasonably well represented in this data set. About 57 per cent of the cases are for the hours between 0700 and noon, and about 40 per cent between noon and 1800. No profiles were measured directly over the city itself, but the number of profiles measured upwind is approximately the same as the number of profiles measured downwind of the city.

All the profiles examined were measured during the month of July, 1976. The aircraft data collected by Dr. M. E. Shauck of Baylor University (see Ludwig, Martinez, and Nitz, 1978) were also investigated, but most of those profiles were collected at higher altitudes and had not been graphed or digitized. Also, the tabulated summaries of Shauck's data had rather poor vertical resolution. For these reasons, it was decided to concentrate the analysis on the data of Westberg et al. (1977), although their data suffers from some of the same deficiencies. In particular, the vertical resolution in the graphical presentations is not as good as was available for the Los Angeles, St. Louis, and Washington, D.C. data sets.

The examples presented in the next section use reproductions of graphs given by Westberg et al. (1977). The reader should be aware that those authors do not always use the same ozone and temperature scales in their graphs. Each vertical profile from Westberg et al. (1977) is accompanied by a map of the Houston area showing the distribution of ozone concentrations observed at the surface. The isopleth analyses in these diagrams are subjective interpretations of the observed values. The winds at the 850-mb level (approximately 1500 m) were determined from the National Weather Service analyses and are shown in the upper right corners of the figures. The wind direction is indicated by an arrow whose length is equal to one hour's travel at the observed speed. Stability classes were determined from the solar radiation and wind data of Westberg et al. (1977) using the algorithm given by Ludwig and Dabberdt (1976). One final note is in order concerning the figures in the following section. The altitude shown on the graphs obtained from Westberg et al. (1977) are given in thousands of feet above sea level (msl).

b. Examples

Figure 33 shows the ozone profile taken about 60 km northwest of Houston during the late afternoon of July 2, 1976. At its highest levels the ozone increased to about 60 ppb. However, up to about 2.4 km

Table 4

SUMMARY OF OZONE PROFILES STUDIED FROM THE HOUSTON AREA

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Approximate Location of Ozone Profile	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760702	1720	1.2	D	4	180	60 km NW	x				A	30	30
760704	1110	0.5	A	3	190	40 km SW	x				A	30	30
760705	1707	0.6	D	5	90	60 km NW	x				F	30	30
760707	0715	0.6	C	4	60	40 km W	x				A	25	35
	0809	1.0	A	4	50	50 km E	x				A	35	35
	0923		A	2	60	50 km NW	x				A	35	35
760708	0740	1.1	B	2	50	30 km W	x				B	15	30
760708	1410	0.6	B	2	200	40 km W	x				F	80	80
760710	1410	0.6	D	7	140	30 km W			x		C	70	50
	1439	0.6	D	7	140	15 km SW			x		C	130	100
760712	0804	0.6	C	4	70	45 km W			x		B	10	35
	1005	1.1	B	5	140	20 km W			x		C	80	80
	1420	1.2	B	4.5	170	50 km W			x		C	160	120
	1610	1.2	C	4.5	170	75 km NW			x		C	170	150
760713	1700	0.9	C	6	190	30 km W	x				F	25	25
760714	1105	0.5	B	2.5	120	35 km W	x				A	30	35
	1535	0.6	C	3.5	190	60 km NW			x		E	80	120
760715	1035	0.6	C	4.5	190	40 km NW			x		F	20	40
	1925		D	2.5	190	45 km W	x				D	20	25
760718	0810	1.1	B	2	190	45 km W	x				D	20	20
760720	0830	0.3	C	4.5	190	35 km W	x				F	25	30
	1640	1.0	C	4.5	150	30 km W			x		D	70	80
760721	0715		C	4.5	100	30 km W			x		B	30	50

Table 4 (Concluded)

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Approximate Location of Ozone Profile	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760722	0805	1.8	A	5	130	35 km W			x		F	25	30
	1215	2.7	A	2.5	140	25 km W	x				A	45	45
760723	0825	1.2	B	0	-	40 km W				x	F	25	25
760724	0930	0.6	B	5	40	35 km W			x		F	35	45
	1400	1.7	B	3.5	180	40 km SW			x		D	80	90
760725	0750	0.6	B	0	-	40 km W	x				B	40	70
	0930	0.3	A	1.5	270	45 km SW	x				F	45	60

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

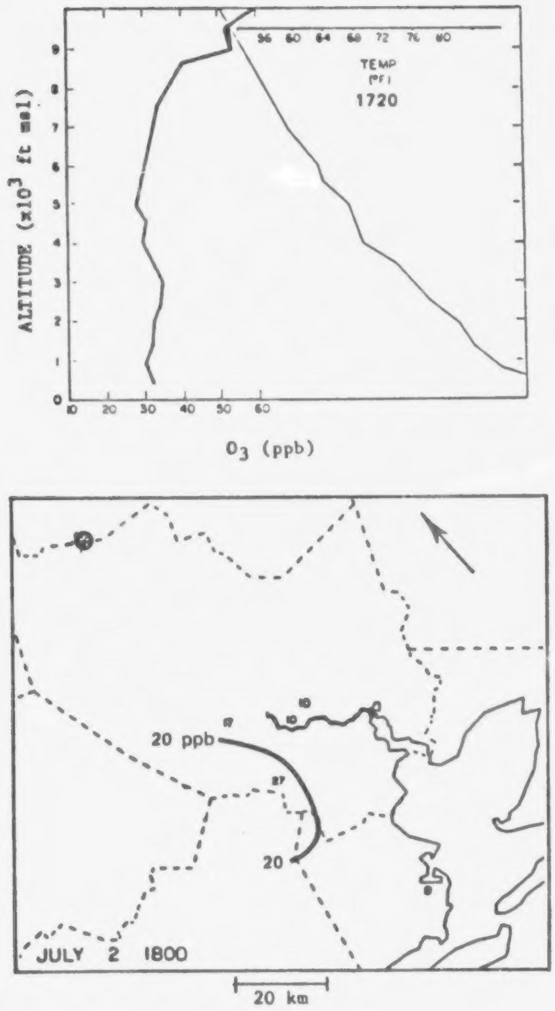


FIGURE 33 HOUSTON OZONE CONCENTRATIONS DURING THE LATE AFTERNOON OF JULY 2, 1976

(8,000 ft), concentrations remain very nearly constant between 30 and 40 ppb, in spite of the fact that there is a stable layer with a base at about 1.2 km (4,000 ft). Thus, the profile has been classified as Type A. Although the 850-mb wind direction suggests that this sounding was made generally downwind of the Houston area, the shape of the ozone profile indicates little or no influence from city emissions, so this profile was not put in the downwind category.

Figure 34 shows another Type A ozone profile, taken near midday on July 4, 1976. The reasons for classifying this as a Type A profile are much the same as those used to classify the July 2 case shown in Figure 33. Ozone concentrations were nearly constant at about 30 ppb, up to an elevation of 2 km (6,500 ft), although there is a strong stable layer at a much lower altitude. This profile was measured slightly upwind, well to one side of the Houston area, and was clearly uninfluenced by Houston emissions.

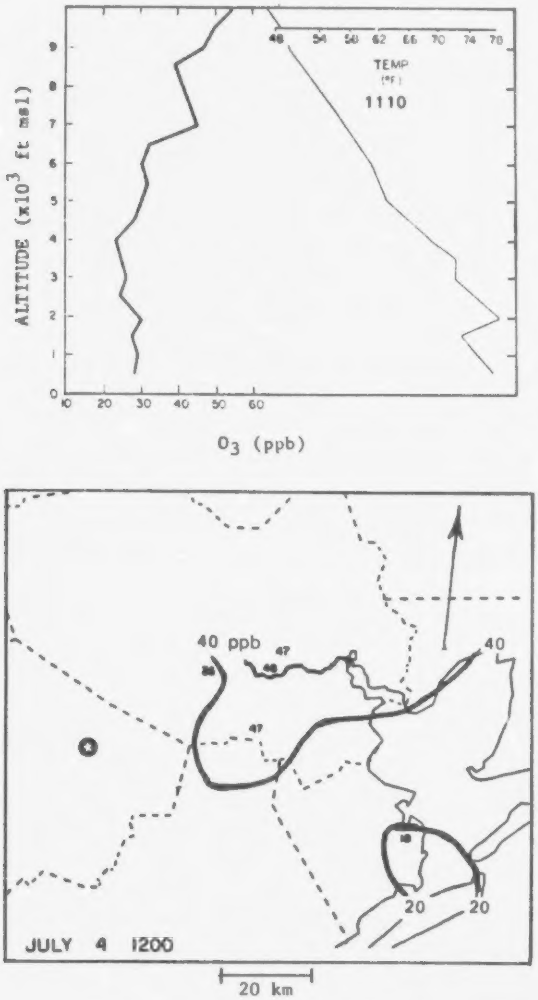


FIGURE 34 HOUSTON OZONE CONCENTRATIONS NEAR MIDDAY OF JULY 4, 1976

The profile shown in Figure 35, for the late afternoon of July 5, 1976, has been classified Type F. Ozone concentrations up to about 2 km (6,500 ft) were nearly uniform at 30 to 40 ppb. This appears to be the height of the afternoon mixing layer, as evidenced by the presence of a nearly isothermal layer in the temperature profile. Above the top of the afternoon mixing layer, the ozone concentrations nearly doubled, to 60 ppb. The profile appears to be little influenced by the Houston emissions, probably from being off to one side, although generally in a downwind direction.

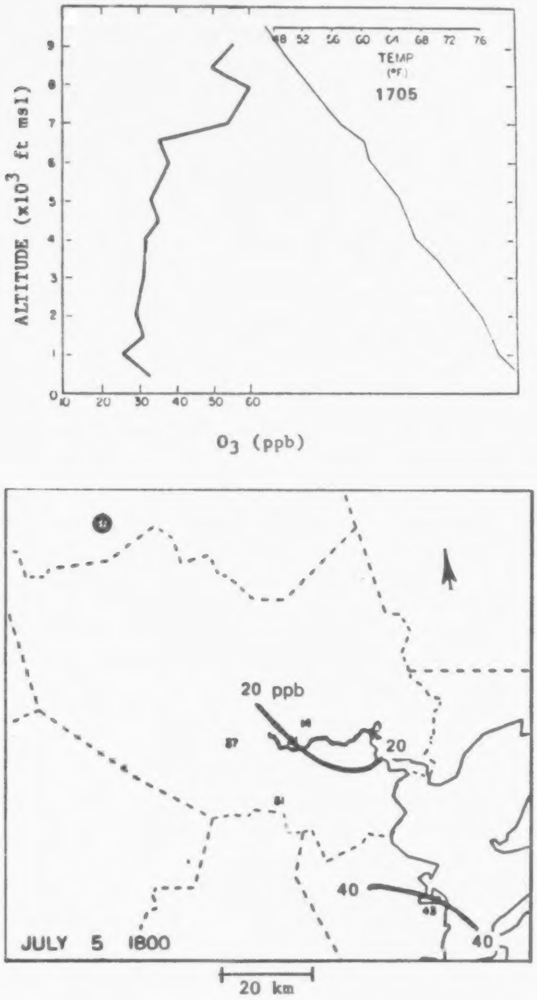


FIGURE 35 HOUSTON OZONE CONCENTRATIONS DURING THE LATE AFTERNOON OF JULY 5, 1976

Figure 36 shows the vertical distributions of ozone at three different times during the morning of July 7, 1976. Although the 850-mb wind direction was from the south to south-southeast during this morning, Table 4 shows that the winds reported by Westberg et al. (1977) at the surface were from the northeast or east-northeast. This probably accounts for the buildup of ozone concentrations to the west of the city. The profile taken at 0715 CST about 40-km west of the city was classified as a Type A profile, although the decrease in concentration near the surface might have warranted a B classification. There was a general, gradual increase in ozone concentration with height from about 35 ppb at around 0.3 km (1,000 ft) to about 55 ppb at about 3 km (10,000 ft). This gradual increase with height is fairly characteristic of the troposphere (Singh, et al., 1977). The other two profiles shown in Figure 36 have also been classified as Type A. They have concentrations between 30 and 40 ppb in the lowest layer, but there are no data above about 1-km (3,300 ft). The earlier sounding that extended to higher altitudes suggests that concentrations at higher altitudes were probably consistent with a Type A ozone profile. None of the profiles shown in Figure 36 appear to have been appreciably influenced by emissions from Houston.

Figure 37 shows ozone concentrations during the morning and afternoon of July 8, 1976. The morning profile was classified as Type B; concentrations above about 0.3 km (1,000 ft) were generally uniform, between about 30 and 40 ppb, but it appears that the concentration at the surface was probably much less than that. During the afternoon of July 8, 1976, ozone concentrations at the surface increased downwind of the Houston and Galveston areas. Concentrations at the surface in the downwind areas exceeded 80 ppb and were even higher aloft, reaching over 100 ppb in a layer between about 0.8 and 1.1 km (2,500 to 3,500 ft). The profiles certainly have the shape of a Type F profile, but the origins of the ozone trapped aloft are unclear. According to Westberg et al. (1977), surface winds during much of the night were calm, so that the pollutants seen in this layer may be the result of precursors emitted during the night and early morning. It is not possible to determine with any certainty the degree to which this profile was influenced by urban emissions, but on the basis of the 850 mb winds and the surface winds near the time of the observation, the profile has been put in the category of those uninfluenced by the urban emissions.

Figure 38 shows an example of a Type C profile. This profile was measured downwind of the Houston area on the afternoon of July 10, 1976. Concentrations at the surface were about 70 ppb. Between about 0.3 and 0.6 km altitude (1,000 to 2,000 ft), ozone concentrations dropped from about 75 to 20 ppb. The 20-ppb concentration coincided with an abrupt change to a more stable lapse rate. Above 0.6 km, ozone concentration increased from about 20 to about 45 ppb at 2.6 km (8,500 ft). The lack of vertical resolution in the data makes it difficult to determine whether the ozone concentrations within the lowest, mixed layer were uniform, but it appears that the sharp decrease in concentration

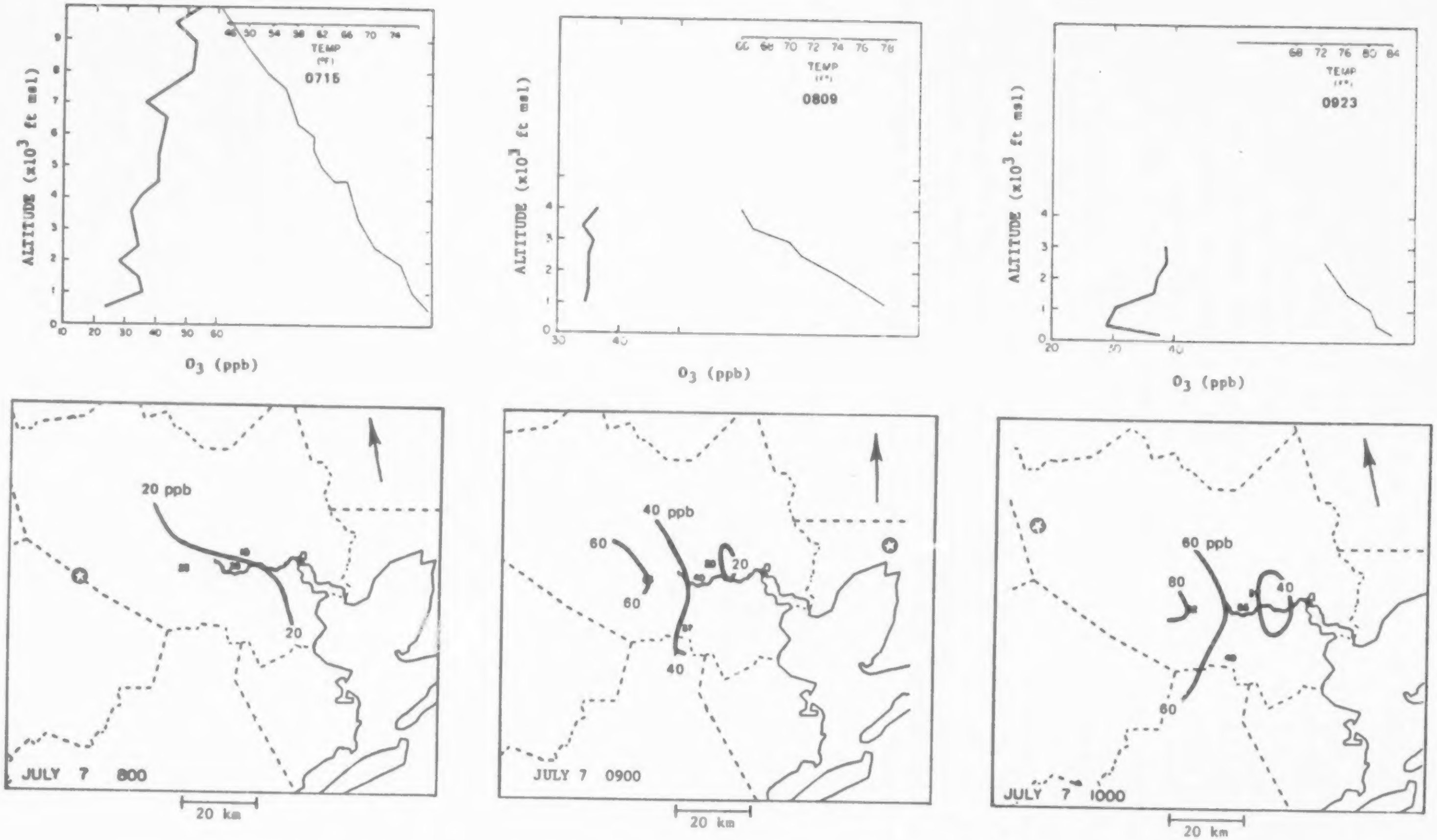


FIGURE 36 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 7, 1976

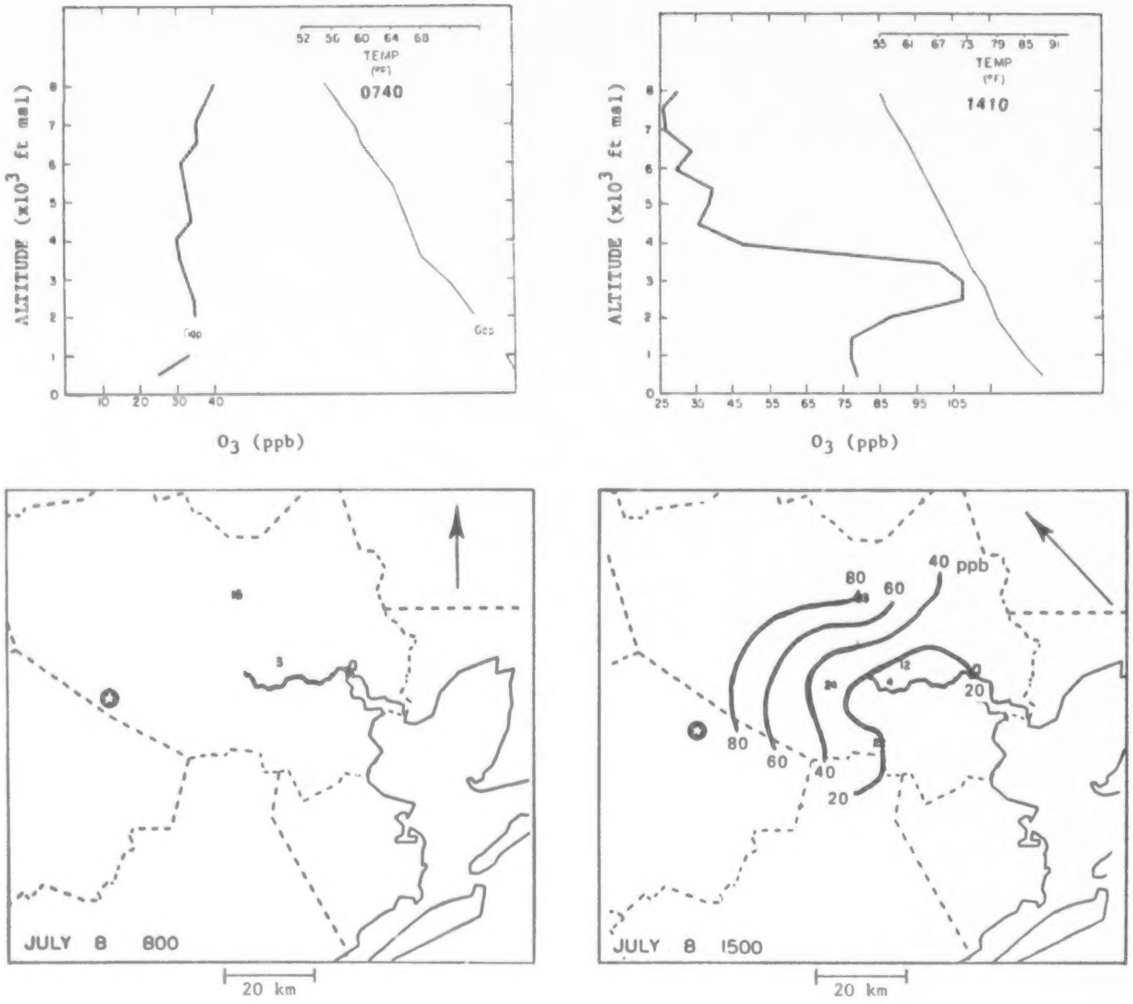


FIGURE 37 HOUSTON OZONE CONCENTRATIONS ON JULY 8, 1976

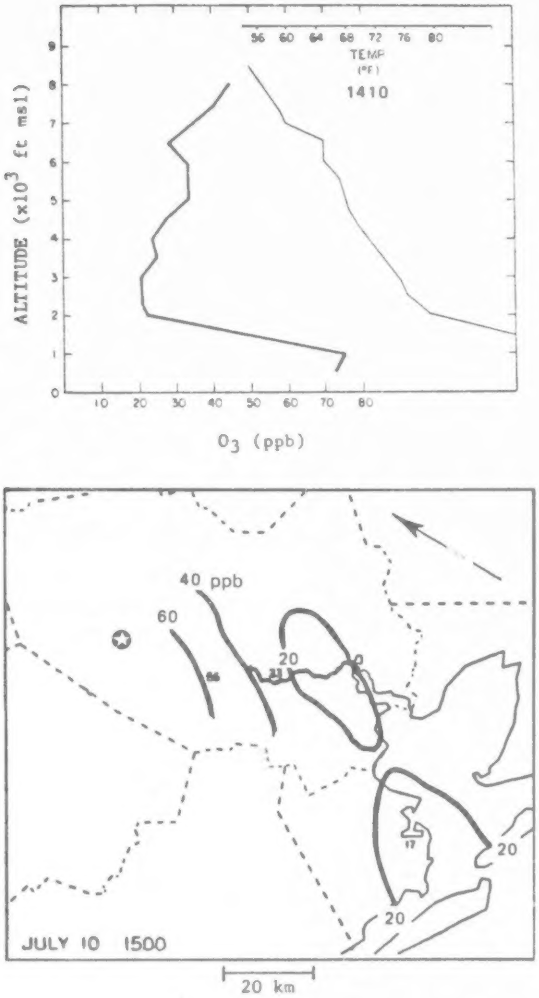


FIGURE 38 HOUSTON OZONE CONCENTRATIONS DURING THE AFTERNOON OF JULY 10, 1976

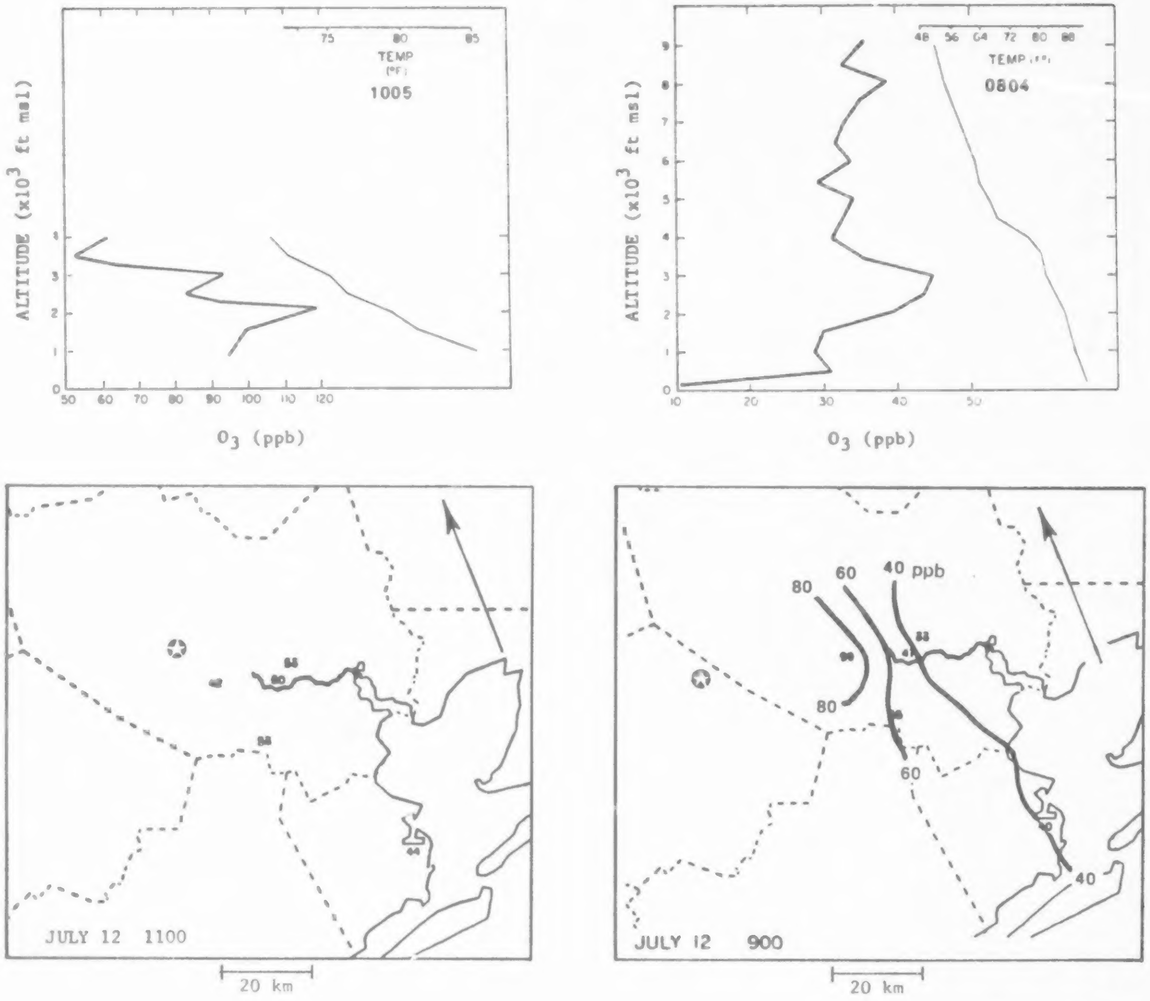


FIGURE 39 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 12, 1976

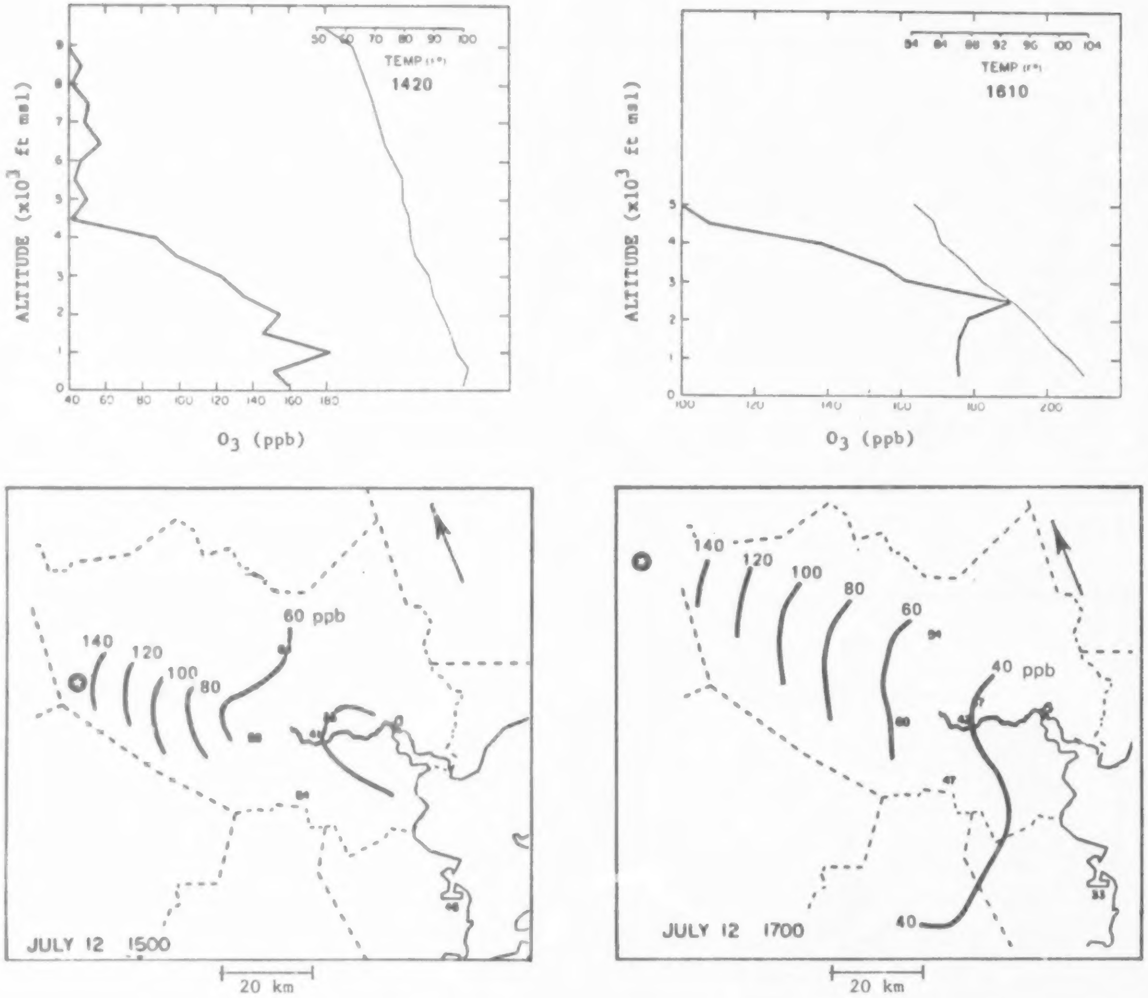


FIGURE 40 HOUSTON OZONE CONCENTRATIONS DURING THE AFTERNOON OF JULY 12, 1976

of the day. However, the vertical ozone profiles taken downwind of Houston, especially during the late morning and during the afternoon, suggest that ground-level ozone concentrations were much greater than those observed in, and upwind of, Houston. The earliest profile was classified as Type B; concentrations at the surface were very much lower than those aloft. The concentrations aloft were generally between 30 and 45 ppb. Concentrations above 1.5 km (5,000 ft) seem to have remained in the 40- to 50-ppb range, at least until afternoon. Figures 39 and 40 show that the concentrations near the surface continued to increase during the day, at least until 1610 CST. However, it does not appear that these high concentrations were uniformly mixed throughout the mixing layer. It is not easy to define the top of the mixing layer from the available data, but it appears to have been around 1.1 to 1.2 km (3,500 to 4,000 ft) after 1000 CST. Thus these profiles show a surface concentration appreciably greater than that observed at the top of the mixing layer; this is an important characteristic of Type C profiles.

Figure 41 shows an ozone profile taken about 30 km west of Houston during the late afternoon of July, 18, 1976. Ozone concentrations observed at ground level generally ranged from about 7 to 13 ppb. Concentrations above about 0.8 km (2,500 ft) were greater, about 50 to 60 ppb. If the temperature profile showed evidence of the formation of a stable layer near the surface, this profile would have been classified as a Type E. However, the category F has been chosen because there appears to be a reservoir of higher ozone concentrations above the mixing layer, but the choice of this category is admittedly very subjective.

Figure 42 shows ozone concentrations during the late morning and the afternoon of July 14, 1976. The sounding made west of the city at 1105 CST shows that concentrations of around 30 ppb extended from near the surface to at least 2.7 km (9,000 ft). Clearly, this is a Type A profile that is generally free of urban influence. Surface concentrations of ozone nearer the urban area reach as high as 100 ppb. The surface winds reported by Westberg et al. (1977) suggest that the precursors emitted in the Houston area moved generally toward the southwest during the morning hours and then, about midday, they turned and moved toward the north. This would have brought the morning precursors, and the ozone formed from them, over the area where the profile was measured at 1535 CST. It is evident that there is considerable ozone within the mixed layer; above the mixed layer the concentrations remained at about 30 ppb, as during the morning hours. Although concentrations were about 150 ppb at an altitude of 0.8 km (2,500 ft), surface concentrations were less than 90 ppb. The temperature profile does not indicate strong stability in the lowest layers, but destruction at the surface appears to have been too rapid to be offset by downward mixing of the ozone aloft. This profile was classified as Type E because there was ozone aloft within the mixing layer and the downward mixing in the lowest layers was not sufficient to offset surface destruction.

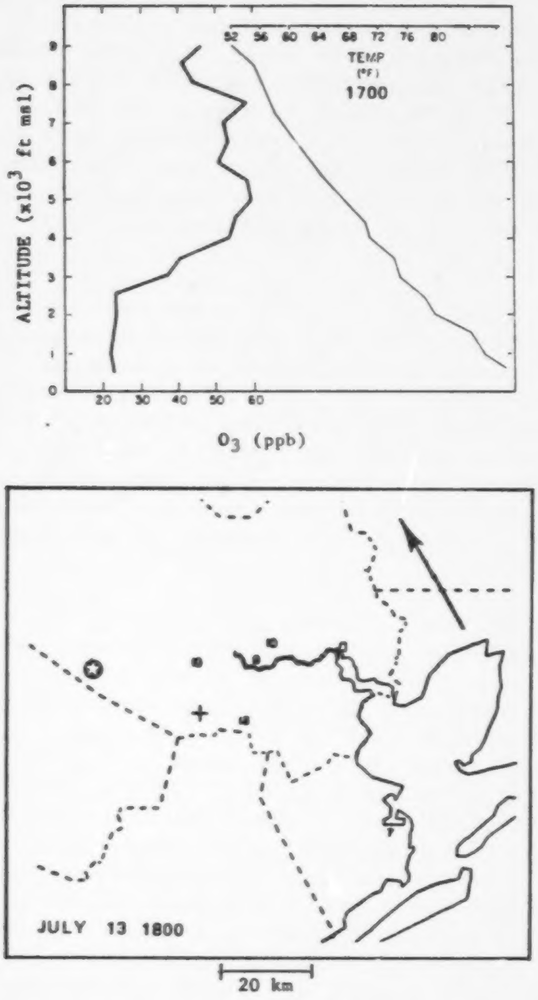


FIGURE 41 HOUSTON OZONE CONCENTRATIONS DURING THE LATE AFTERNOON OF JULY 13, 1976

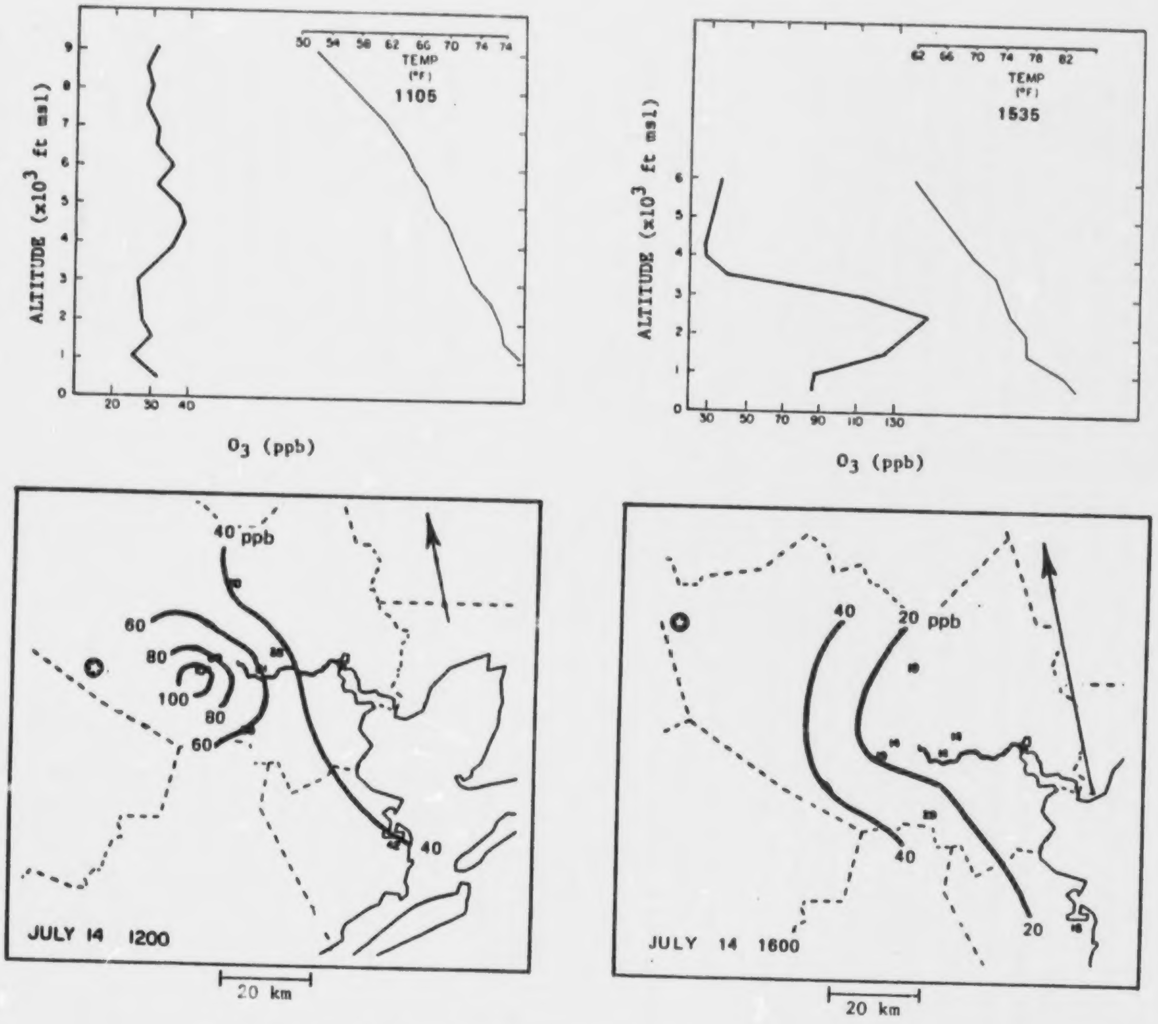


FIGURE 42 HOUSTON OZONE CONCENTRATIONS, JULY 14, 1976

Figure 43 shows the ozone concentrations in the late morning and early evening of July 15, 1976. The morning profile, taken at 1035 CST, shows that there was a layer of higher ozone concentration associated with a more stable portion of the temperature profile, at about 0.8 to 0.9 km (2,500 to 3,000 ft). Ozone concentrations observed at the surface were quite low throughout the area, generally less than 30 ppb. These concentrations are consistent with the lower portions of the vertical profiles. The 1035 CST profile has been classified as a Type F because of the ozone layer aloft. By early evening, 1925 CST, ground-level ozone concentrations had fallen below 20 ppb everywhere in the area. In most places close to the city, the concentrations were near zero. The vertical profile about 45 km west of the city suggests that ground-level concentrations were about 15 ppb. At higher altitudes, the ozone concentrations were about 20 to 30 ppb and relatively uniform to the top of the sounding. If we knew that these same concentrations continued upward above the height to which afternoon mixing had penetrated, we could confidently classify this profile as Type A. However, it has been classified as Type D because we do not know whether the same concentrations were found above the afternoon mixing layer.

Figure 44 shows morning ozone concentrations around Houston for July 18, 1976. Although there appears to be an isothermal layer at the surface, the ozone concentrations were no less there than at higher altitudes. The concentration is uniform at 20 ppb from the surface up to the elevated stable layer at about 1.1 to 1.4 km (3,500 to 4,500 ft). Concentrations above this altitude increase slightly to about 30 ppb. It is uncertain what the concentrations were above the profile, so it was classified as Type D; it would probably be equally easy to justify a Type A classification.

Figure 45 shows ozone concentrations during the morning and afternoon of July 20, 1976. The 0830 CST profile is Type F. Mixing had not proceeded to very high altitudes and so the concentrations of ozone aloft are much greater than those at the surface. There is some evidence that the mixing may have been more pronounced within the city, and hence there are greater ozone concentrations at the surface, 40 to 60 ppb in the city versus about 25 ppb where the profile was measured. Similarly, there may have been greater mixing over the warm water surfaces to the southeast of Houston, where a surface ozone concentration of 60 ppb was observed. Figure 45 shows that by afternoon, considerable ozone had been formed within the mixing layer. Ozone concentrations of 75 to 85 ppb were found from the surface to 1.1 km (3,500 ft). The 1640 CST profile seems to have been influenced by the emissions from the city, but there are other areas more directly downwind where concentrations at the surface exceeded the 100 ppb.

Figure 46 shows the ozone concentrations around Houston during the morning of July 21, 1976. The profile taken west of the city at 0715 CST shows that concentrations above 0.8 km (2,500 ft) were generally 50 to 65 ppb. No profile data are available below 0.8 km, but extrapolating

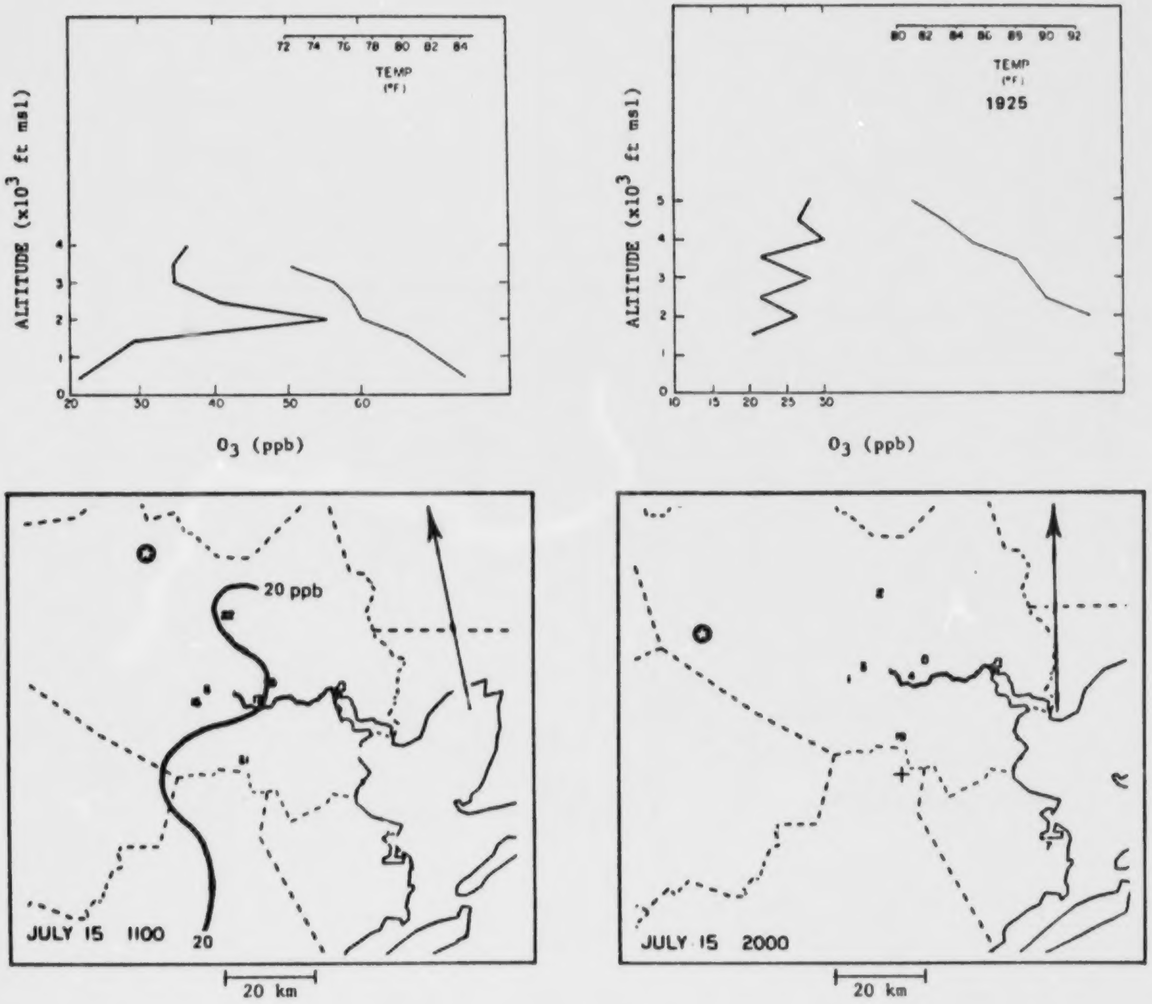


FIGURE 43 HOUSTON OZONE CONCENTRATIONS ON JULY 15, 1976

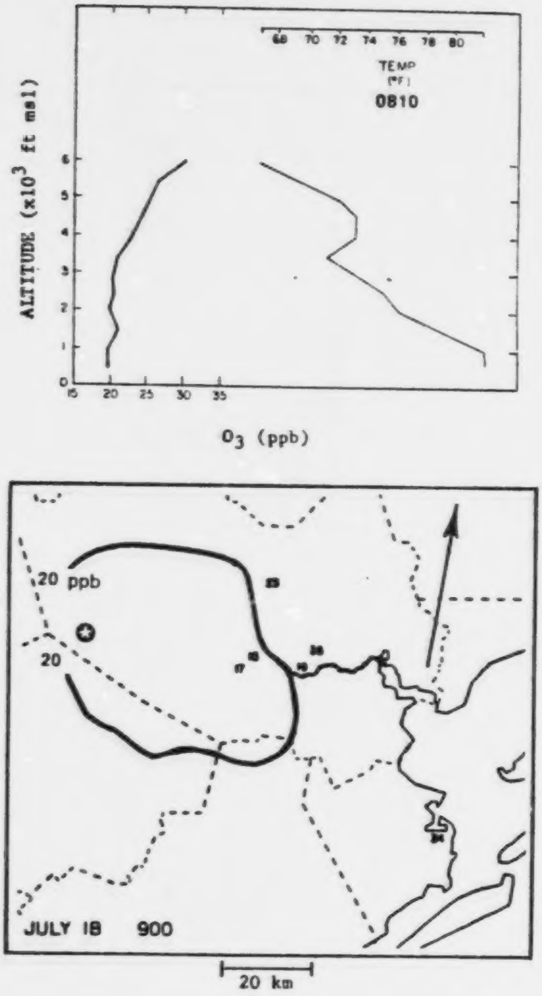


FIGURE 44 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 18, 1976

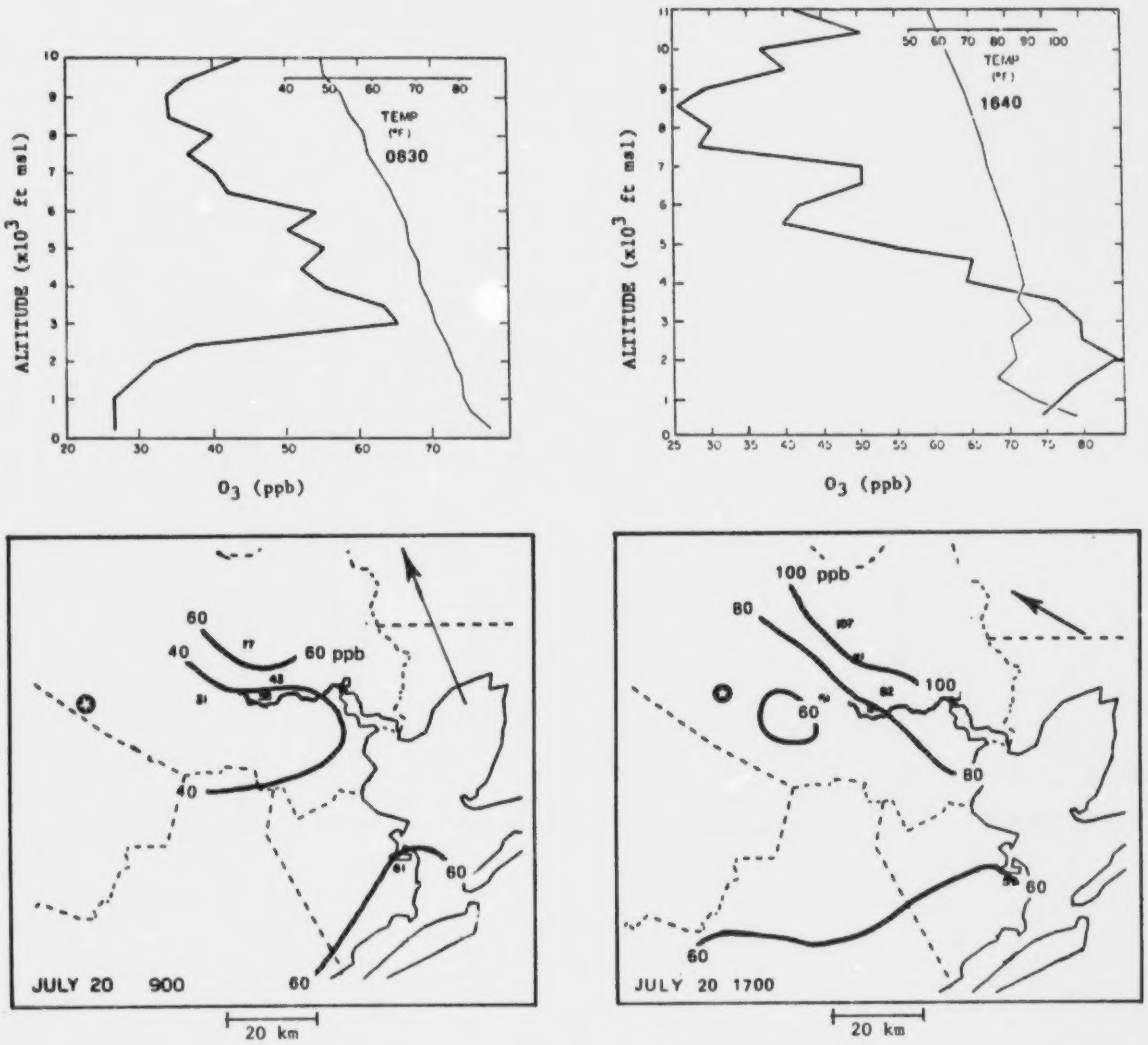


FIGURE 45 HOUSTON OZONE CONCENTRATIONS ON JULY 20, 1976

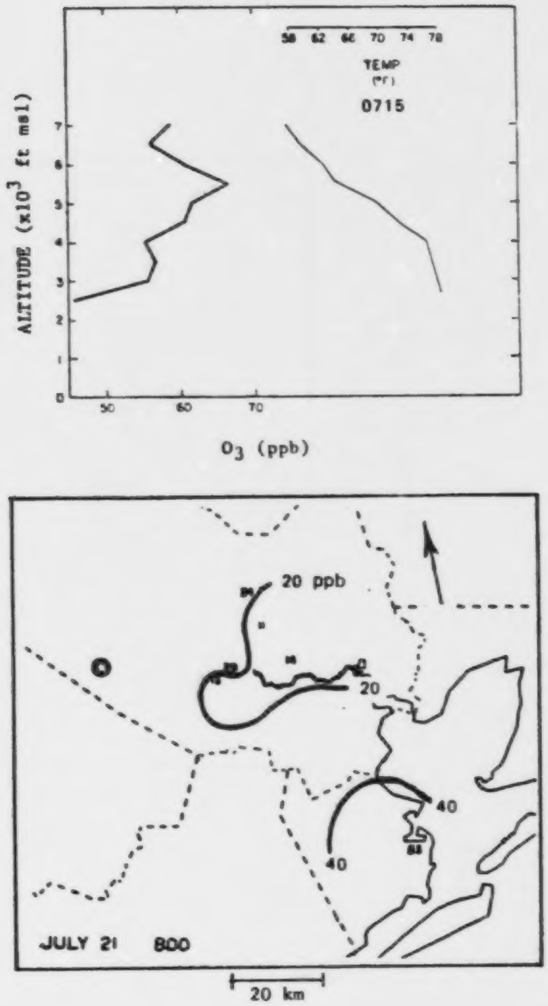


FIGURE 46 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 21, 1976

the analysis of the surface observations suggests that the concentration near ground level was around 20 ppb. It is not unreasonable to expect that the thermal stratification in the lower layers was fairly stable at this early hour. Therefore, vertical mixing was probably inhibited and the destruction of ozone at the surface was probably not offset by downward mixing from aloft, making this a Type B profile.

Figure 47 shows the ozone concentrations during the morning and at about midday on July 22, 1976. During the morning (0805 CST), concentrations were 25 to 30 ppb from the surface up to about 1.7 km (5,500 ft). The winds reported earlier in the morning at ground level by Westberg et al. (1977) were calm. Some ozone may have remained aloft in the relatively stable layer above 1.7 km, making this a Type F profile. The midday (1215 CST) profile is a Type A profile; concentrations were between 40 and 50 ppb from the surface up to an altitude of at least 2.7 km (9,000 ft). The location where the profile was measured was uninfluenced by the emissions from the city; downwind of the city, concentrations exceeded 160 ppb.

Figure 48 shows the ozone concentrations during the morning of July 23, 1976. The profile of this morning was very similar to that on the preceding morning. Concentrations were around 25 ppb below the isothermal layer at 1.2 km (4,000 ft). They were more than 55 ppb at higher altitudes. The profile has been classified as Type F because of the greater ozone concentrations above the mixed layer. The generally calm winds reported by Westberg et al. (1977) suggest that the air throughout the lowest layers was relatively stagnant and may have been influenced by the nearby urban area, but this is uncertain.

Figure 49 shows morning and afternoon concentrations on July 24, 1976. The morning profile, taken downwind of the city, shows relatively low concentrations at the surface, around 35 ppb. There were higher concentrations aloft, about 60 to 75 ppb. Trajectory calculations and the very light surface-pressure gradients prevailing in the gulf coast area at this time indicate that there was probably considerable "milling around" of the air with an accompanying accumulation of urban precursor emissions. It appears from Figure 49 that the greatest ozone concentrations at the surface were found to the southeast of the Houston area at this time. However, this may reflect enhanced mixing over the warmer water surfaces during the morning. Such mixing would have brought ozone down to the surface from aloft. Under light wind conditions, virtually the entire area has to be considered as having been influenced by urban precursors. During the afternoon, the ozone profile shows near uniform concentrations of 85 to 105 ppb throughout the mixed layer. Above the mixed layer, ozone concentrations were in the 70-ppb range.

Figure 50 shows the ozone concentrations on the morning of July 25, 1976. At 0750 CST, the temperature profile shows that the lowest layers were reasonably stable. An analysis of surface ozone observations suggests that the surface concentration was around 40 or 50 ppb in the lowest layers. The profile shows ozone concentrations of about 60 to 75 ppb above the lowest layers, appreciably more than the concentrations at ground level, making this a Type B profile. Somewhat later in the morning, at 0930 CST, there was evidence of mixing in the lower layers at the site where the profile was taken, to the southwest of Houston. Above the mixed surface layer was a stable layer with a base at 0.3 km (1,000 ft). Within the stable layer, ozone concentrations of 80 ppb were observed; within the surface-based mixed layer, the concentrations rose

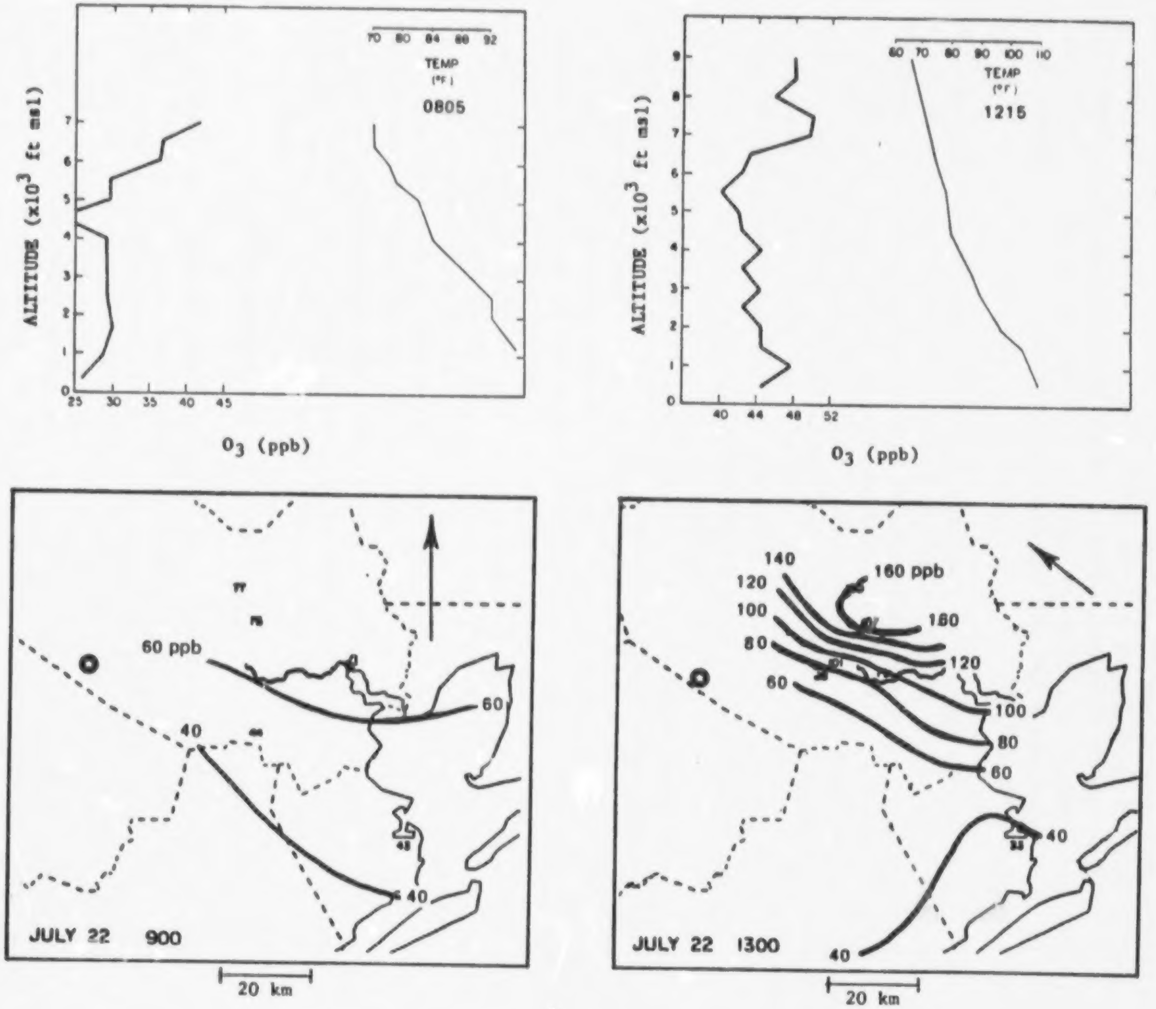


FIGURE 47 HOUSTON OZONE CONCENTRATIONS ON JULY 22, 1976

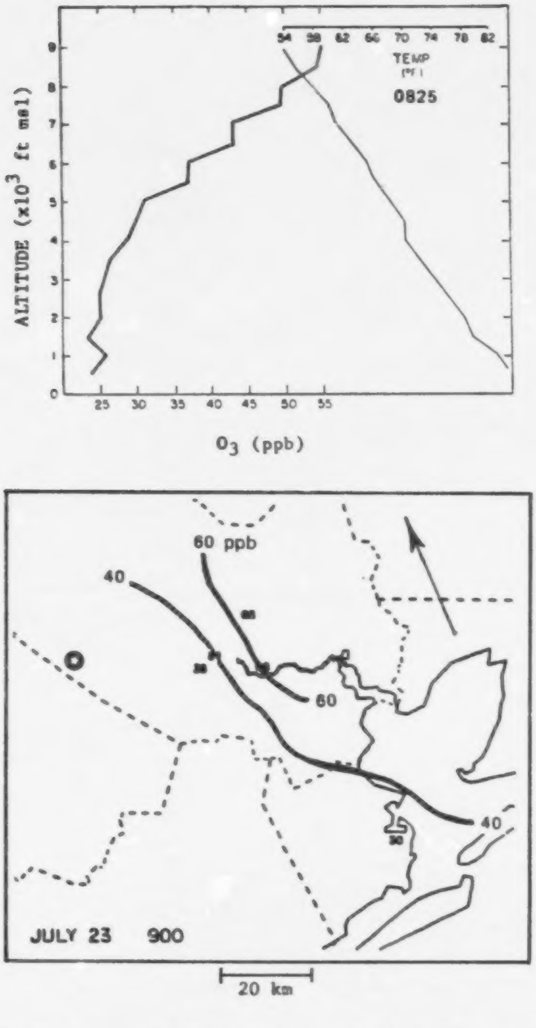


FIGURE 48 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 23, 1976

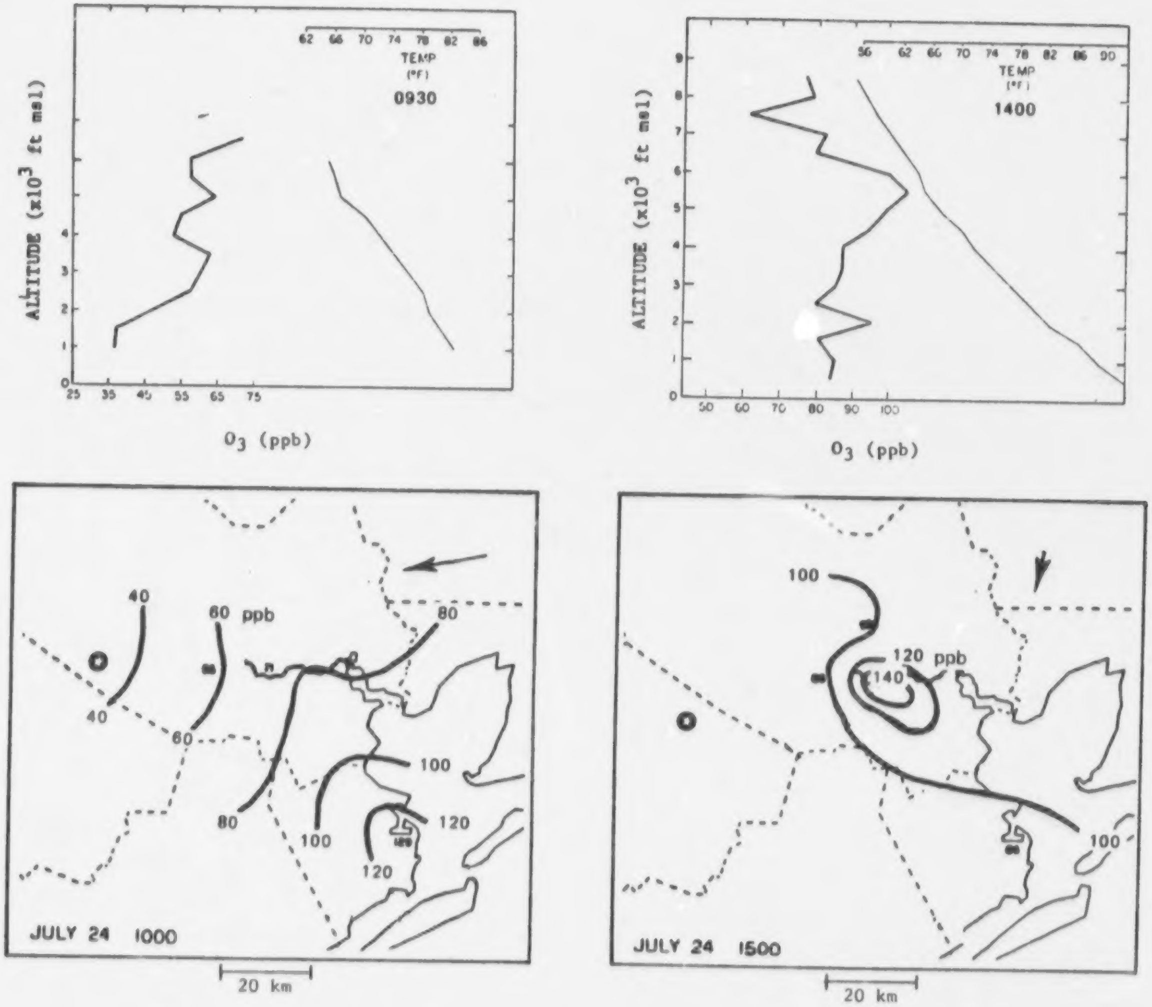


FIGURE 49 HOUSTON OZONE CONCENTRATIONS ON JULY 24, 1976

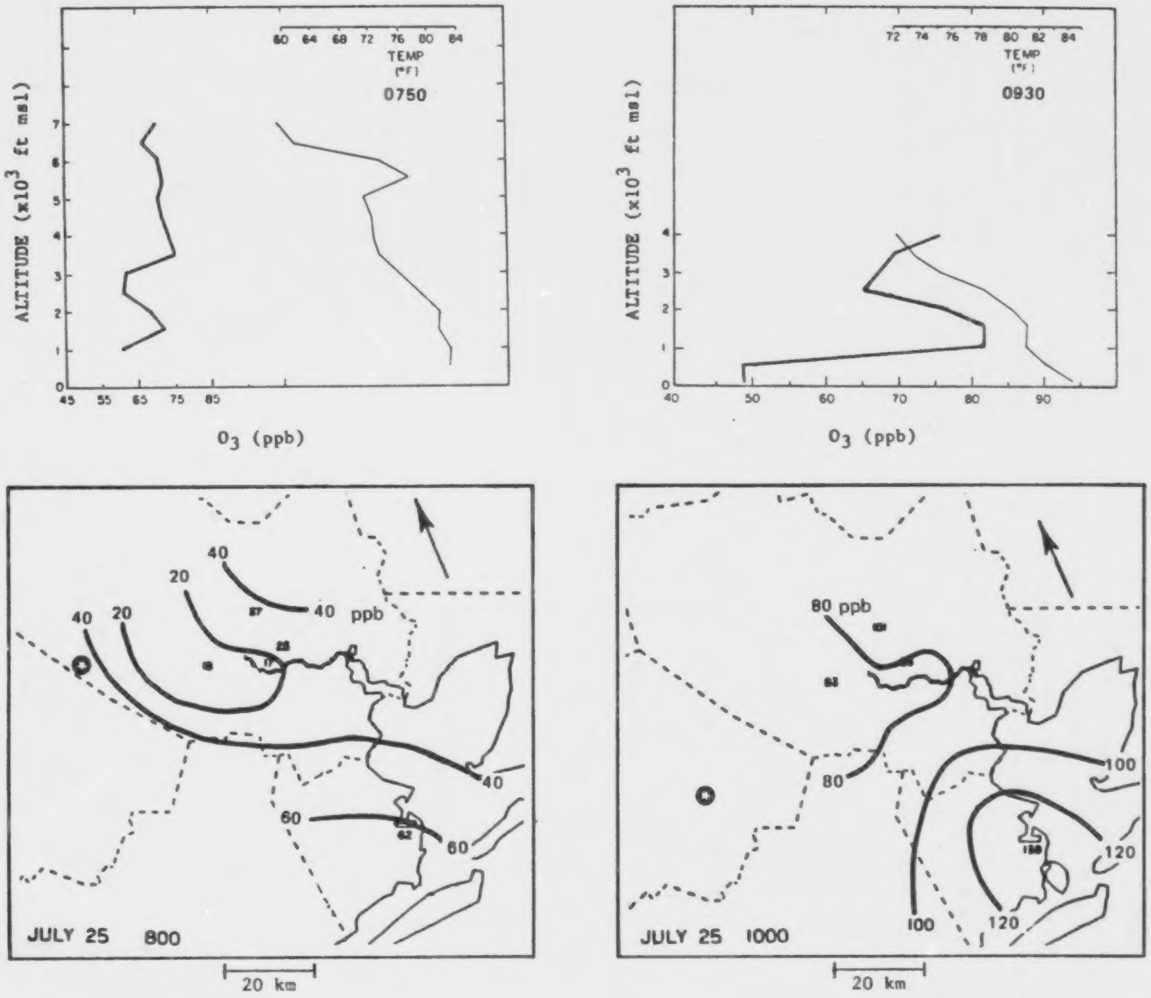


FIGURE 50 HOUSTON OZONE CONCENTRATIONS DURING THE MORNING OF JULY 25, 1976

from a value at the surface of about 50 ppb to the 80 ppb within the stable layer. A profile like this, indicating higher concentrations of ozone stored in a stable layer aloft is a Type F profile.

The presence of such an ozone layer aloft is generally an indication of pollutant effects from the preceding day. The light and variable winds prevailing on this and the preceding day make it quite possible that the ozone concentrations measured aloft anywhere in the area might have come from anthropogenic and other emissions during the preceding day or so. Figure 51 shows the trajectories of the air arriving at Houston on August 24-25, 1976. The air had remained within 200 km of Houston for an extended period of time, so there was probably considerable accumulation of pollutants, but the locations where the two profiles were taken on the morning of July 25, 1976, seem to be reasonably free of very recent urban influence.

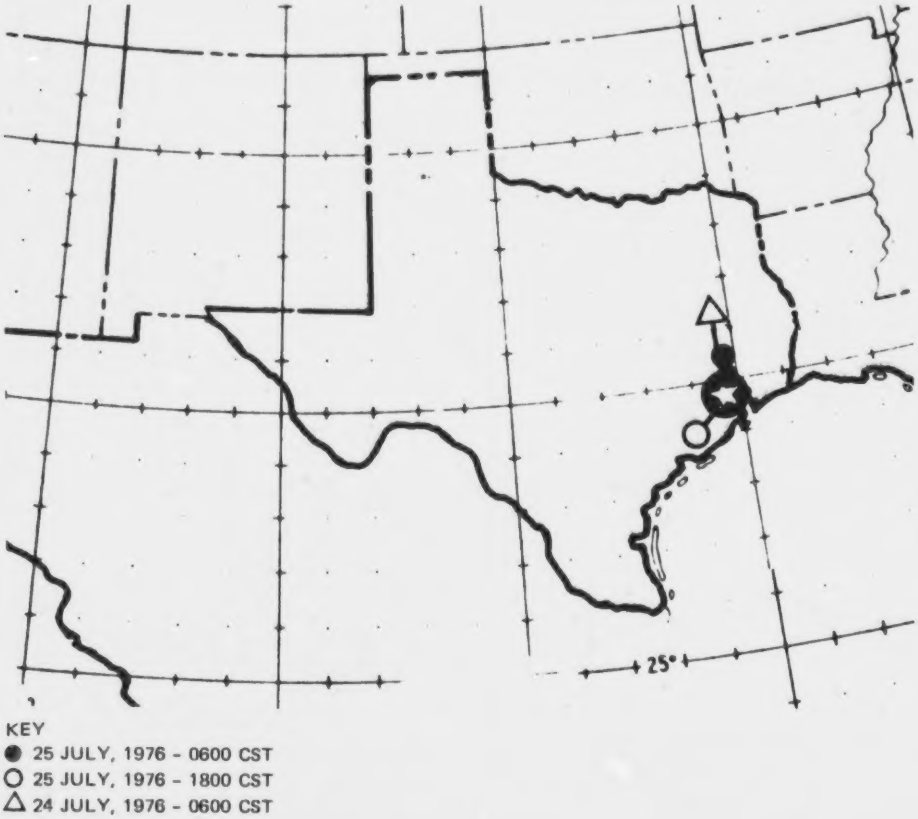

25°
KEY
● 25 JULY, 1976 - 0600 CST
○ 25 JULY, 1976 - 1800 CST
△ 24 JULY, 1976 - 0600 CST

FIGURE 51 LOCATION 48 HOURS EARLIER OF AIR ARRIVING IN HOUSTON ON JULY 24-25, 1976

4. Washington, D.C.

a. Background

Table 5 summarizes the 31 profiles available from the Washington, D.C. area. The data provide a good balance between morning and afternoon cases. Twelve profiles are for the hours between 0600 and 1200 EST, and 19 cases come from the hours between 1200 and 1900 EST.

Unfortunately, the surface ozone observations available from the area did not provide very wide coverage. Most of the available data come from the urbanized parts of Washington and Baltimore. However, flight restrictions prevented any profiles from being measured over the central part of the cities themselves, so it was difficult to combine surface and aircraft data. Flight restrictions also prevented the aircraft from obtaining data at the lowest altitudes, generally below 500 m. The lack of surface and low-altitude measurements makes interpretation of some of the profiles somewhat uncertain. Counterbalancing these shortcomings is the fact that many measurements were made during a period of prolonged stagnation. Thus, these data from Washington, D.C., provide a good picture of the buildup of ozone within the mixing layer during stagnant conditions.

The winds at 850 mb (approximately 1500 m, msl) were determined from the National Weather Service analysis and are indicated by arrows plotted on the maps accompanying the ozone profiles shown in the next section. The length of the arrows represents one hour's travel distance, except where dashed arrows are shown. In those cases, the winds were too light to be displayed in the same way; one hour's travel time would usually be less than the length of the arrow head.

The surface winds shown in Table 5 were estimated from the surface weather map analyses of the National Weather Service. The estimates of stability class shown in Table 5 were derived from wind and cloud cover information contained in these same analyses, using Turner's (1964) algorithm. The ozone profile types and the surface ozone concentrations shown in Table 5 have been estimated largely on the basis of the upper parts of the profiles measured, and by use of the kinds of reasoning that went into the development of the profile classification system.

b. Examples

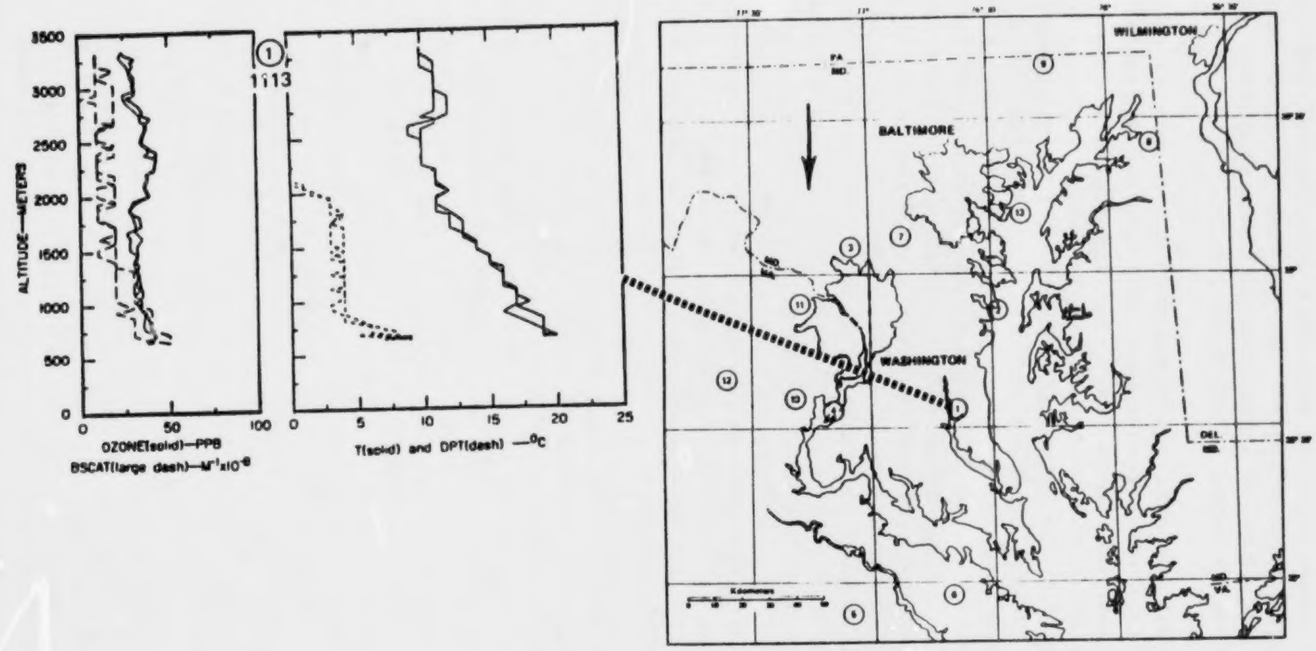
Figure 52 shows the ozone profile measured to the southeast of Washington, D.C., during the late morning of August 17, 1976. The two lines shown in the graph indicate that measurements were made during both an ascending and a descending spiral, as was usually the case in the Washington data set. The temperature and dew point profiles indicate that there was very good mixing up to the base of a stable layer at about 2500 m. The ozone concentrations were nearly uniform, about 40 ppb, throughout the mixed layer and above. In the lowest layers, there

Table 5

SUMMARY OF OZONE PROFILES STUDIED FROM THE WASHINGTON, D.C., AREA

Date	Time (EST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (As shown in Figs. 52-62)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760817	1113	1.8	B	2.5	330	1			x		A		40
760818	0921	0.8	D	7.5	30	2	x				A	40	40
	0940	1.6	D	7.5	30	3			x		A	30	40
	1008	1.5	D	7.5	30	4	x				A	40	40
	1031	1.6	D	7.5	30	1	x				A	50	40
	1648	2.0	D	5	60	4			x		D	100	90
	1711	1.8	D	5	60	1	x				D	90	100
	1750	1.8	D	5	60	5	x				C	90	70
	1810	2.1	D	5	60	6	x				C	90	75
	1843	2.0	D	5	60	2	x				D	90	100
760819	0955	0.8	C	5	50	8	x				F	30	35
	1019	0.7	C	5	50	9	x				F	30	40
	1047	1.0	B	5	50	7			x		F	30	40
	1109	1.8	B	5	50	10			x		A	40	50
	1625	1.6	D	5	90	8	x				D	90	70
	1645	1.8	D	5	90	9	x				D	80	70
	1711	1.8	D	5	90	7			x		C	100	80
	1743	2.0	D	5	90	10			x		C	110	90
760820	0636	0.5	C	2	360	7			x		E	10	40
	0703	0.5	C	2	360	4			x		E	10	50
	1620	1.5	C	2.5	150	7	x				D	110	110
	1644	1.3	C	2.5	150	4	x				D	90	90
	1726	1.4	C	2.5	150	8	x				C	100	85
	1745	1.3	D	2.5	150	9	x				D	90	85
760821	1210	0.9	B	2.5	70	7			x		D	110	100
	1232	1.0	B	2.5	70	11			x		D	120	110
	1251	1.2	B	2.5	70	12			x		D	90	100
	1318	0.9	B	2.5	70	1				x	D	100	100
	1343	0.8	B	2.5	70	13				x	C	190	125
760823	0640	0.4	D	2.5	360	7				x	A	60	60
	1636	0.9	D	5	320	7				x	D	70	70

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral



AUGUST 17, 1976

FIGURE 52 WASHINGTON, D.C. OZONE PROFILE, 1113 EST, AUGUST 17, 1976

are some indications that concentrations of light-scattering particles near the surface were greater than aloft. No similar indications are seen in the ozone profile, so it has been classified as a Type A profile. The 850-mb winds indicate that this location was downwind of Baltimore; the surface winds suggest it was downwind of Washington. In either event, it was probably influenced by urban emissions and was therefore classified as being downwind of a city.

Figure 53 shows the data collected during the morning of August 18, 1976. Spiral ascents and descents were made at four different locations around the Washington-Baltimore area. All the profiles show ozone concentrations of about 40 ppb throughout their entire vertical extent. The earliest data, for the sounding ending 0921 EST, indicate that a stable layer was present near the surface, with its top below 1000 m. The dew point trace suggests that the moisture is confined to this layer, but that aerosols, as indicated by the nephelometer (Bscat) readings, were mixed to levels above 1500 m. Similarly, at the other locations, the nephelometer profiles show the top of the layer with the greatest aerosol concentrations to be at 1500 to 1600 m. In general, the temperature profiles also indicate the same height for the top of the mixed layer. Apparently the ozone that was present was mixed rather thoroughly through a much greater depth of the atmosphere, and little or no new ozone formed from precursors confined within the mixing layer. Only the 0940 EST profile that was taken southwest of Baltimore seems likely to have been influenced by precursor emissions from a nearby urban area, but even it shows little or no sign of excess ozone formation within the mixed layer.

Figure 54 shows the measurements taken at five locations during the late afternoon and early evening of August 18, 1976. There are many important differences between the profiles shown in Figure 54 and those shown for the same morning in Figure 53. The most important of these differences is the buildup of ozone, presumably formed from precursors within the mixed layer. In three of the five locations, the ozone concentrations are reasonably uniform throughout the depth of the mixed layer. The two profiles taken farthest from the urban area show relatively high concentrations at the lowest altitude; the concentrations decreased with height through the mixed layer. These latter two profiles are of Type C; the other three are Type D. According to the surface winds and the winds aloft, none of the profile locations should have been influenced appreciably by urban emissions from nearby cities during the afternoon of August 18, 1976, except perhaps for the profiles taken at the southern edge of Washington at 1648 EST.

Figure 55 shows the trajectories of the air arriving at Washington, D.C., on August 18, 1976, as calculated by Mr. Dale Coventry of the Environmental Protection Agency using Heffter and Taylor's (1975) computerized trajectory program. The air arriving in Washington, D.C., had passed over most of the urbanized areas along the east coast, so it is quite likely that a considerable amount of ozone precursors had been injected into the atmosphere and that those precursors and the ozone

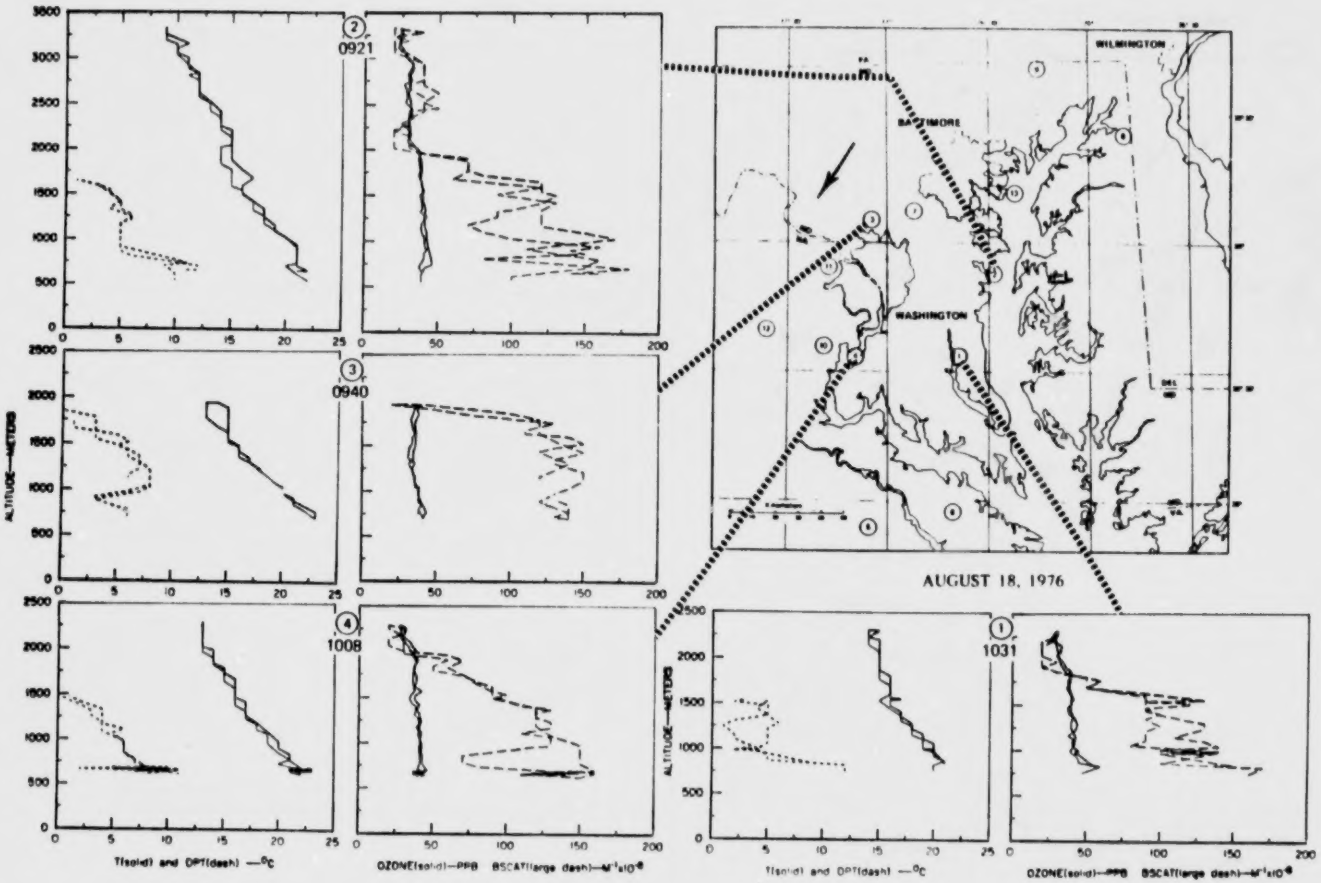


FIGURE 53 WASHINGTON, D.C. OZONE PROFILES DURING THE MORNING OF AUGUST 18, 1976

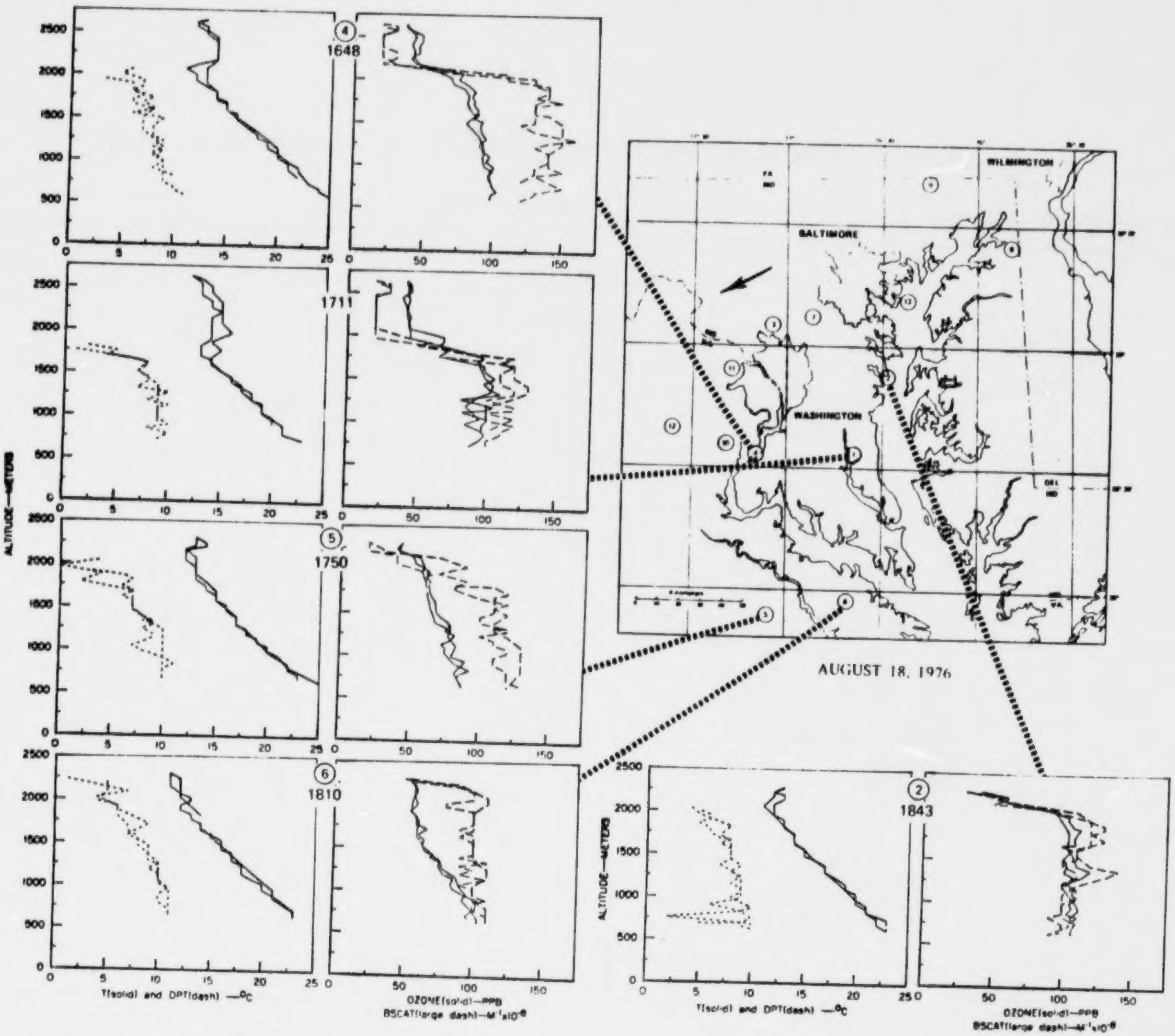


FIGURE 54 WASHINGTON, D.C. OZONE PROFILES DURING THE LATE AFTERNOON OF AUGUST 18, 1976

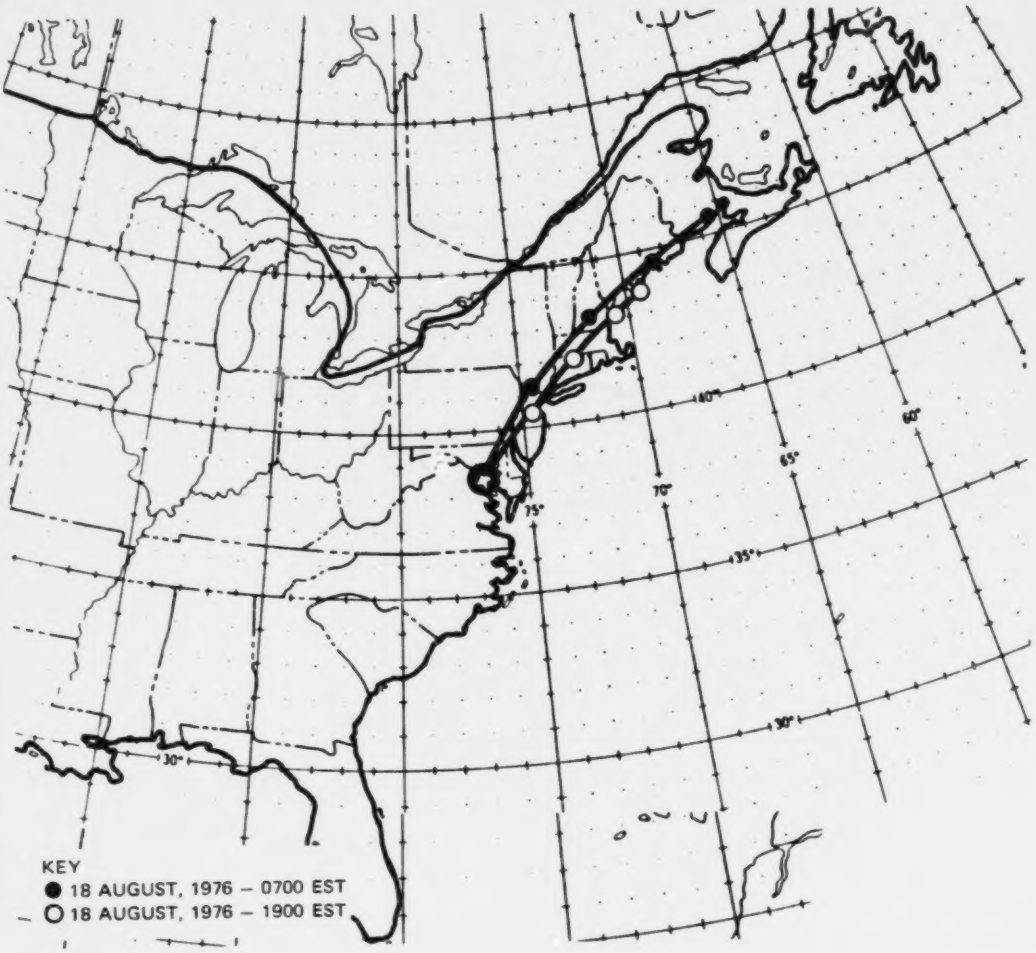


FIGURE 55 TRAJECTORIES OF AIR ARRIVING AT WASHINGTON, D.C. ON AUGUST 18, 1976 AT 0700 AND 1900 EST

formed from them were reasonably uniformly mixed through the depth of the mixing layer. There is no apparent explanation for the two southernmost profiles, where the ozone is not uniformly mixed through the mixing layer.

Figure 56 shows the ozone profiles measured around the Washington-Baltimore area on the morning of August 19, 1976. The three more northerly ozone profiles, measured before 1100 EST, are all of Type F. In each case, there was a layer between about 800 and 1200 m where concentrations exceeded 50 ppb. Below this layer, concentrations were around 30 ppb; it appears that mixing has not proceeded to the point where this elevated layer has been eroded. The profile measured downwind of Washington, D.C., at 1109 EST also shows some very slight signs of an

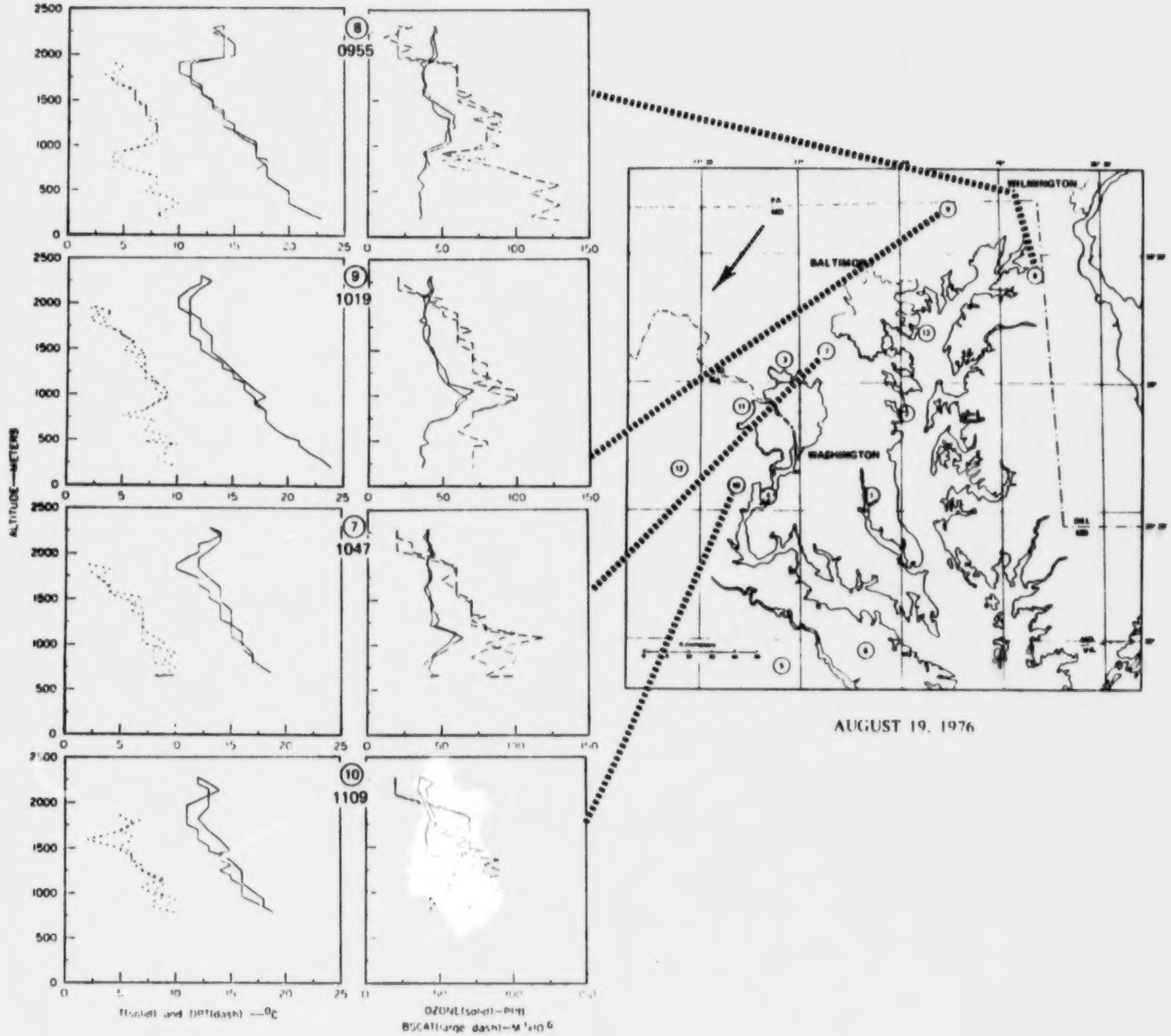


FIGURE 56 WASHINGTON, D.C. OZONE PROFILES DURING THE MORNING OF AUGUST 19, 1976

elevated layer, but concentrations were much more nearly uniform at 40 ppb.

Figure 57 shows the ozone profiles during the afternoon of August 19, 1976. The two upwind profiles taken to the northeast of Baltimore are typical Type D profiles with nearly uniform concentrations of 70 to 80 ppb up to the top of the mixed layer, at about 1600 to 1800 m. The upper parts of the profiles taken downwind of Baltimore (at 1711 EST) and downwind of Washington (at 1743 EST) are very similar to the upper parts of the upwind profiles. However, at the lower altitudes, downwind concentrations were appreciably greater, being 100 ppb or more near the surface. This appears to have been the effect of ozone produced from urban precursors that had not mixed thoroughly throughout the mixing layer. These profiles have both been classified as Type C.

Figure 58 shows ozone profiles measured south of Washington and between Washington and Baltimore early on the morning of August 20, 1976. All the available surface observations of ozone concentrations in Baltimore and Washington, D.C., as well as those from two stations to the northwest of Baltimore, show that concentrations at ground level were less than 10 ppb at this hour. This almost certainly reflects the effects of a stable layer at the surface, which probably formed during the night. It appears that the ozone concentrations increased with height from near zero values at ground level to more than 70 ppb in the air above the ground-based inversion. Above the base of the elevated inversion that was present at about 1300 m, the ozone concentrations were 30 to 40 ppb. Winds were very light throughout the layer below 1500 m; as shown in Figure 58, the morning 850-mb wind was very light from the east and the surface wind was very light from the north (see Table 5). Both profiles were taken downwind of urban areas, but at the early hour at which they were taken, there had not been sufficient photochemical activity to produce any discernible effects in the lower parts of the ozone profiles.

Figure 59 shows conditions in the Washington area during the afternoon of August 20, 1976. A strong subsidence inversion was evident throughout the area at around 1300 to 1400 m. Winds within the mixed layer were very light and from the east-southeast. Figure 60 shows that air arriving at Washington, D.C., during the early evening of August 20, 1976, had come from the east at a rather slow rate of speed. The dots on the trajectory mark the air position at 12-hour intervals; during the preceding 48 hours, the air had traveled only about 450 km. The generally uniform distribution of the 100-ppb ozone concentrations below the subsidence inversion indicates that the mixing was fairly good. The nature of the nephelometer and the ozone traces indicates that very little material was mixed upward out of the layer below the inversion. A restriction to upward diffusion and the slow air movement allowed enough precursors to accumulate in the lowest layers to produce the 100-ppb ozone concentrations observed.

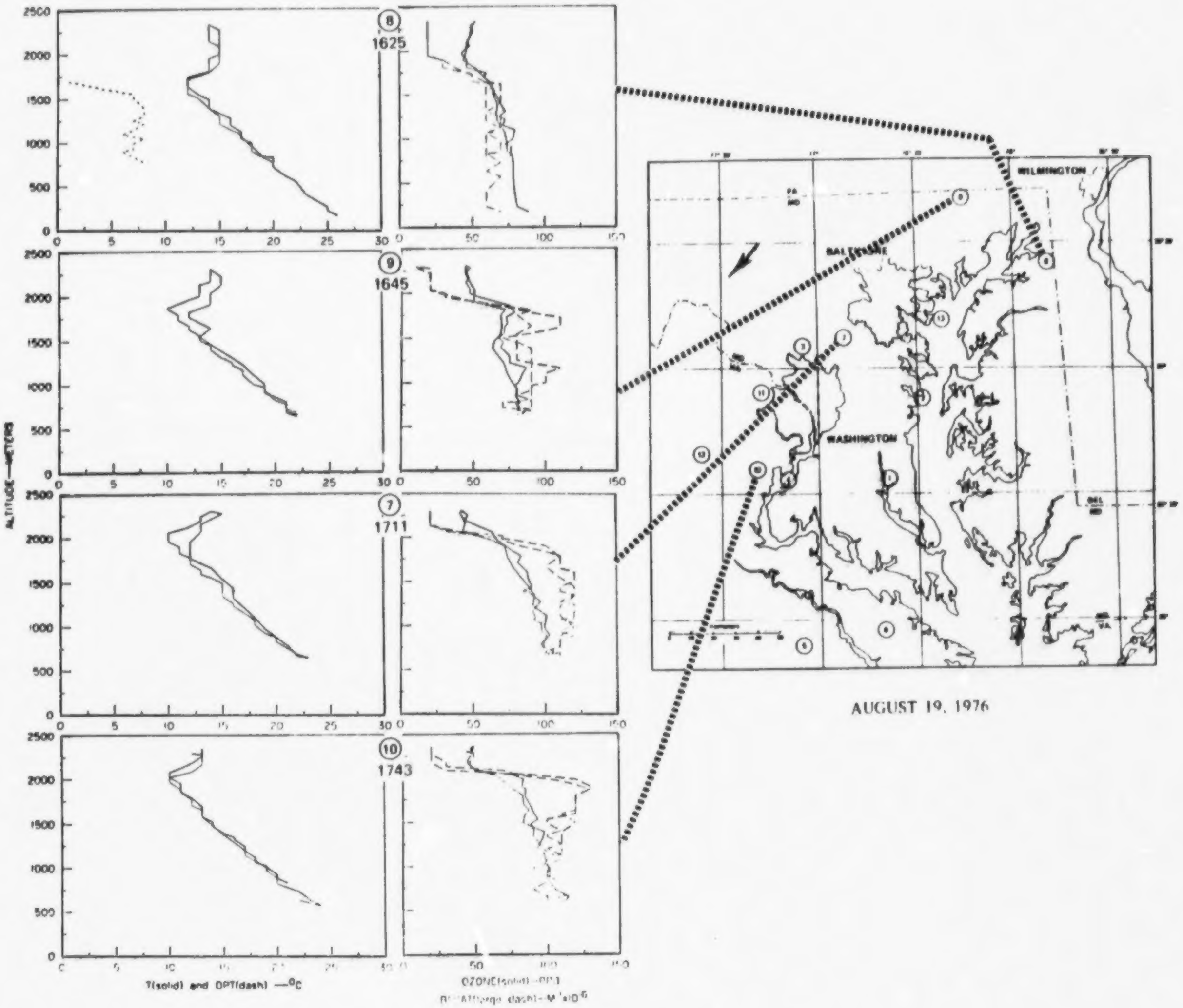


FIGURE 57 WASHINGTON, D.C. OZONE PROFILES DURING THE AFTERNOON OF AUGUST 19, 1976

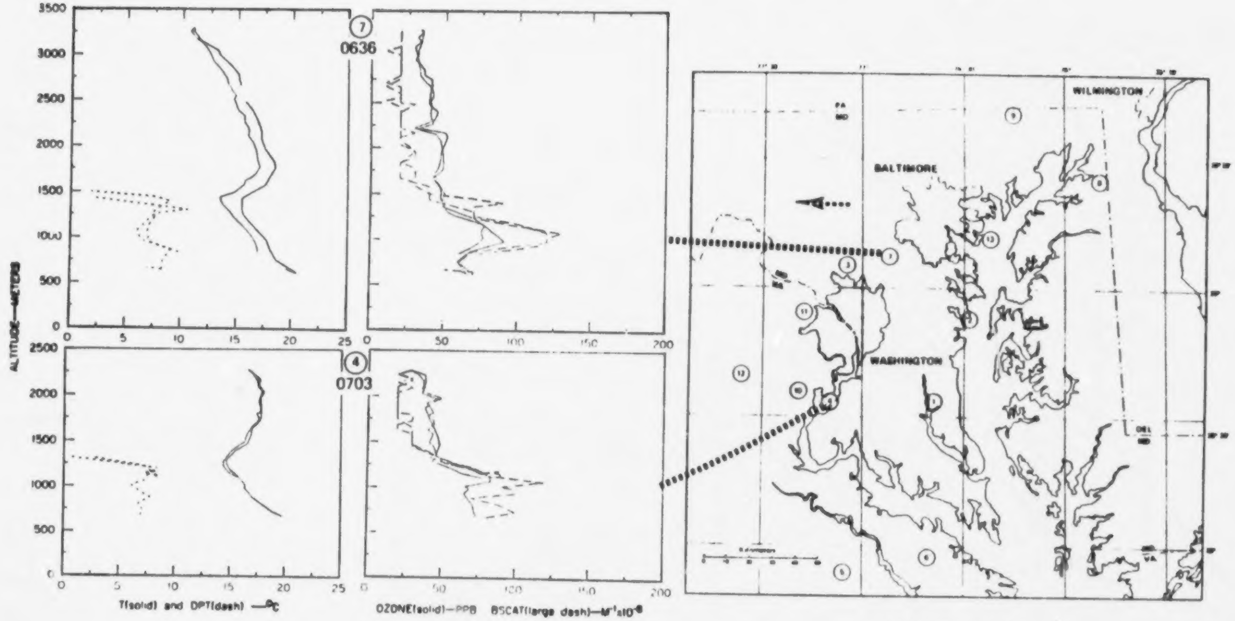


FIGURE 58 WASHINGTON, D.C. OZONE PROFILES DURING THE MORNING OF AUGUST 20, 1976

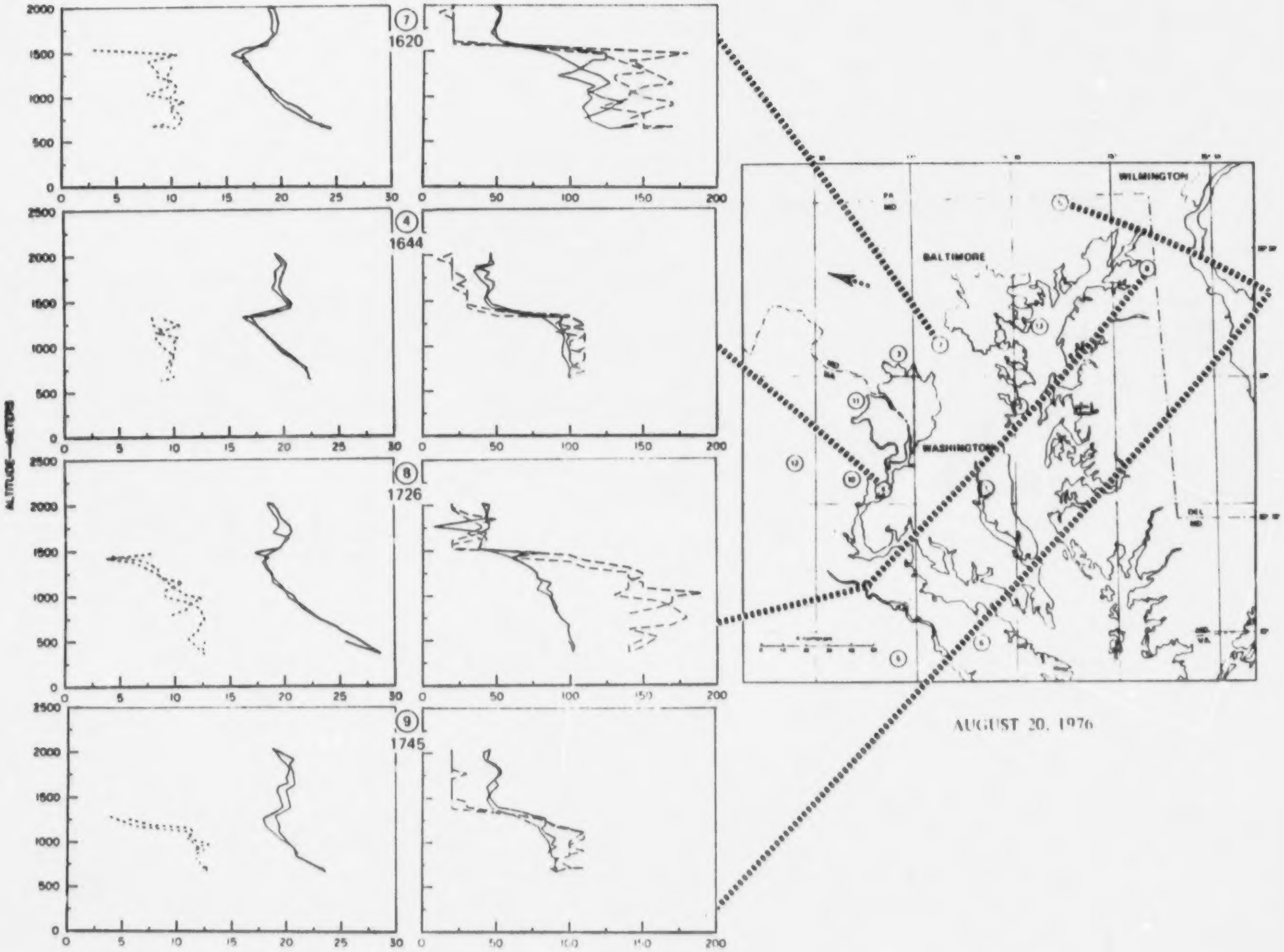


FIGURE 59 WASHINGTON, D.C. OZONE PROFILES DURING THE LATE AFTERNOON OF AUGUST 20, 1976

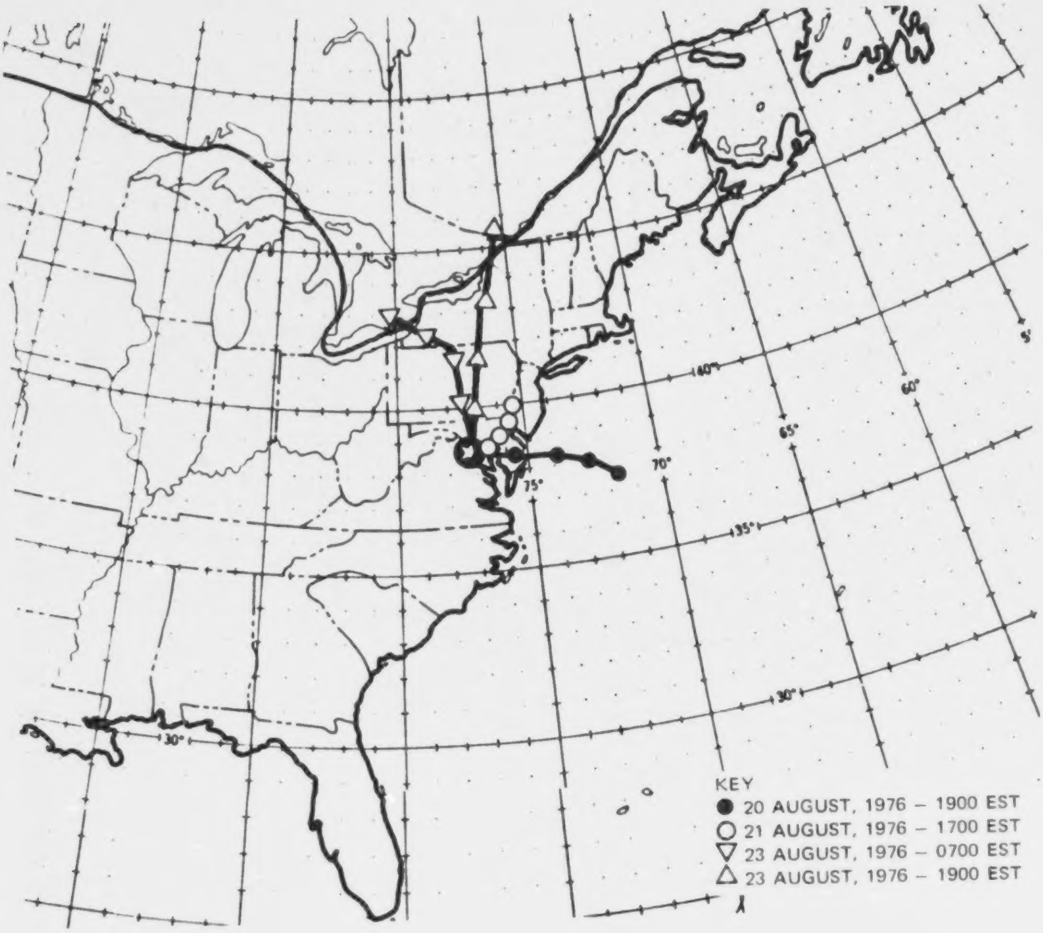
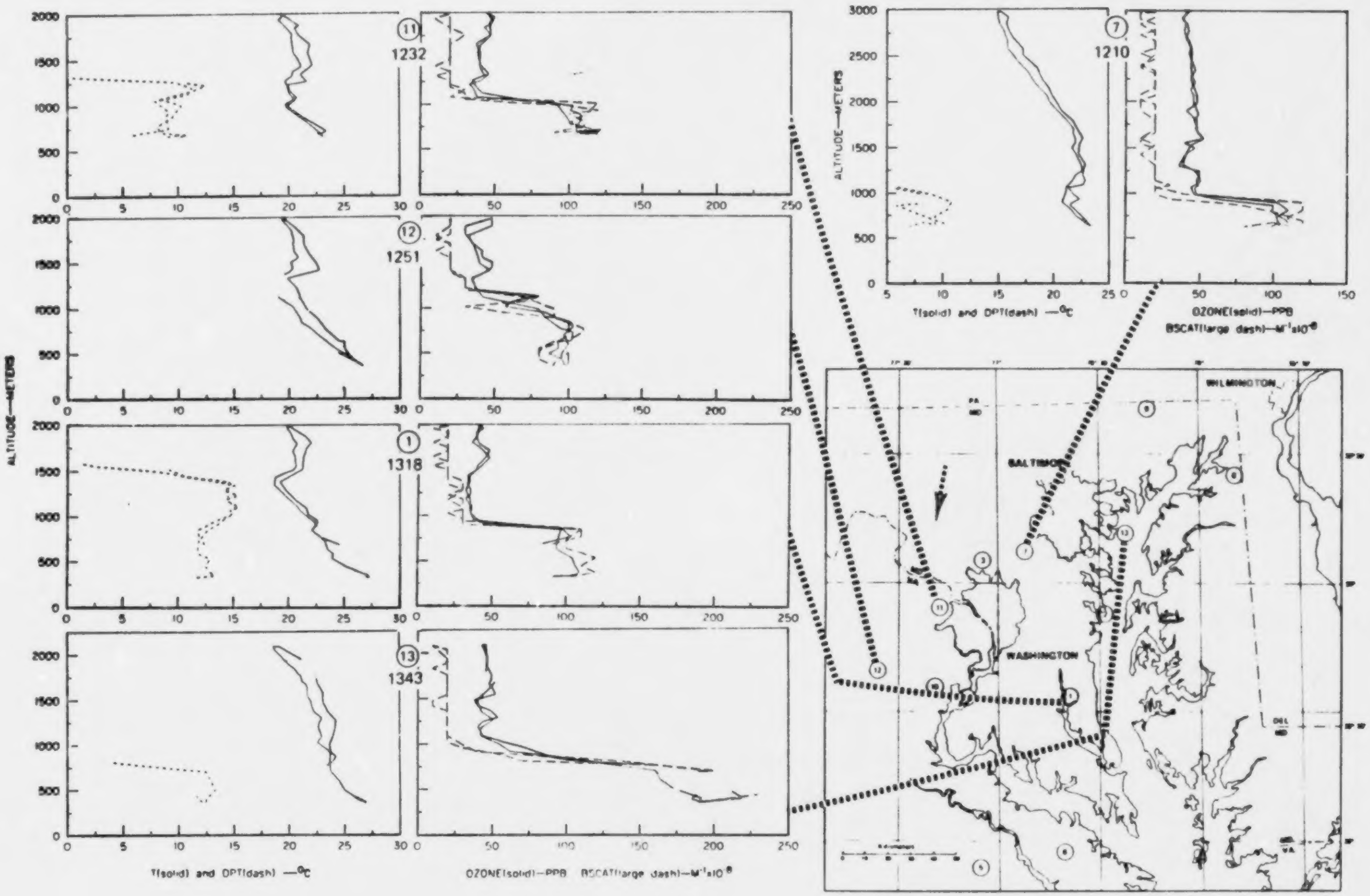

KEY
● 20 AUGUST, 1976 – 1900 EST
○ 21 AUGUST, 1976 – 1700 EST
▽ 23 AUGUST, 1976 – 0700 EST
△ 23 AUGUST, 1976 – 1900 EST
140°
135°
30°
30°
75°
70°
65°
60°

FIGURE 60 TRAJECTORIES OF AIR ARRIVING AT WASHINGTON, D.C. ON AUGUST 20, 1900 EST; AUGUST 21, 1700 EST; AND AUGUST 23, 0700 AND 1900 EST, 1976

The light winds and near-stagnant conditions persisted in the Washington area through the following day, August 21, 1976. Ozone concentrations remained high and were confined below the subsidence inversion, as can be seen in Figure 61. This figure shows ozone concentrations shortly after midday on August 21, 1976. Figure 60 shows that air arriving in Washington, D.C., during the morning had come from the north and had traveled only slightly more than 200 km during the preceding two days. Most of the profiles show ozone concentrations to have been about 100 ppb throughout the depth of the mixing layer. Ozone concentrations measured over the water to the east of Baltimore at 1343 EST were appreciably higher, approaching 200 ppb in the lowest layers. Although the



AUGUST 21, 1976

FIGURE 61 WASHINGTON, D.C. OZONE CONCENTRATIONS AT ABOUT MIDDAY ON AUGUST 21, 1976

wind measurements indicate otherwise, this profile gives evidence of the recent addition of urban precursors.

Figure 62 shows two ozone profiles measured between Washington and Baltimore during the morning and afternoon of August 23, 1976. The 850-mb winds were very light, from approximately north in the morning and shifting to north northwest during the late afternoon. The trajectories of the air arriving at Washington, D.C., on this day are shown in Figure 60. These two profiles illustrate the evolution of a Type A profile, as observed in the morning, into a Type D profile as the precursors contained within the mixed layer are converted to ozone. The light winds make it very difficult to determine the extent to which these profiles were influenced by urban emissions. However, it seems likely that if there had been great influence, the ozone concentrations in the afternoon would have exceeded the 70 ppb that was observed.

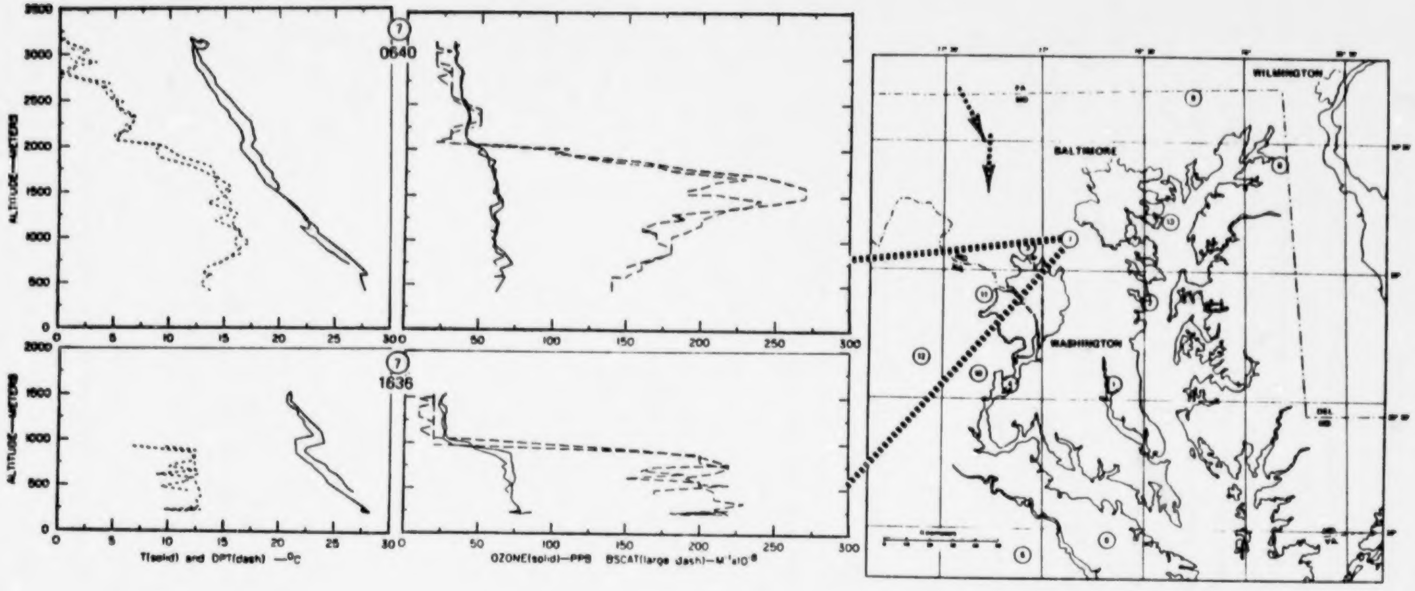
c. Other Areas

The preceding section presented many examples of vertical profiles of ozone and other photochemical pollutants in the four primary study areas. The intention in presenting so many individual profiles, with the accompanying discussions of the factors considered when classifying those profiles, was to show how the various physical processes had to be considered in order to classify the data. The numerous examples were also intended to show the kinds of uncertainties inevitably encountered when a subjective classification scheme is applied to the real world. With those objectives accomplished, it is sufficient to present tabulated summaries of the vertical profiles as observed in other areas from which data are available. The data discussed below have been combined with those from the primary study areas in order to develop some statistical descriptions of the combined data sets. For example, the relative frequencies of the various kinds of profile have been determined for different periods of the day and for different locations relative to the city. The statistical summaries are discussed later.

5. Toronto

Table 6 summarizes the Toronto area ozone profiles that were classified. The classified profiles were obtained from the report of Wiebe, Lusis and Anlauf (1975). All the data were collected near Toronto, over Lake Ontario or near Niagara, during August of 1975. All 53 profiles were measured during daylight hours, between about 0800 and 1700 EST. The forenoon accounted for 20 of the profiles, the afternoon for the remaining 33.

Figure 63 is a map of the area in which the Toronto ozone and temperature profiles were measured. The important locations referred to in Table 6 are shown on the map. The winds given in the table are generally estimated from those observed with pilot balloons in the lowest



AUGUST 23, 1976

FIGURE 62 WASHINGTON, D.C. OZONE PROFILES, AUGUST 23, 1976

Table 6

SUMMARY OF OZONE PROFILES STUDIED FROM THE TORONTO AREA

Date	Time (EST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 63)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
750808	1206	1.0	A	1	240	Toronto Island				x	F	75	60
	1233	0.7	A	1	240	Lake Ontario				x	A	45	55
	1245	1.1	A	1	240	Niagara				x	C	40	55
	1450	1.2	A	1	240	Toronto Island				x	D	70	90
	1512	1.2	A	1	240	Lake Ontario				x	D	85	90
	1545	0.3	B	1	240	Niagara				x	D	120	110
750809	1130	1.2	B	5	200	Toronto Island	x				D	125	115
	1150	1.1	B	5	200	Lake Ontario	x				D	125	130
	1210	1.2	B	5	200	Niagara	x				D	115	110
	1527	1.5	B	3	190	Toronto Island	x				D	135	130
	1545	1.4	B	3	190	Lake Ontario	x				D	155	130
	1604	1.4	B	3	190	Niagara	x				D	145	130
750810	1125	0.4	B	3.5	180	Toronto Island	x				C	105	105
	1155	0.4	B	5	180	Niagara	x				D	80	90
	1435	1.5	C	4	160	Toronto Island	x				D	130	90
	1455	0.5	C	3	150	Niagara	x				A	105	90
750811	1035	0.2	D	4	210	Toronto Island	x				E	65	80
	1105	0.2	D	4	210	Niagara	x				A	75	80
	1316		D			Toronto Island	x				C	120	100
	1343		D			Lake Ontario	x				D	115	100
	1353		D			Niagara	x				D	125	95
750812	0947	0.3	A	2	170	Toronto Island	x				E	35	60
	1001	0.3	A	2	170	Niagara	x				E	45	60
	1015	0.5	A	2	170	Lake Ontario	x				E	50	75
	1103	0.4	A	1.5	170	Toronto Island	x				E	85	115
	1117	0.5	A	1.5	170	Niagara	x				E	85	110
	1130	0.4	A	2.5	160	Lake Ontario	x				E	55	80
	1405	0.2	B	3.5	170	Toronto Island	x				D	110	110
	1430	0.2	B	4	160	Lake Ontario	x				F	55	55

Table 6 (Concluded)

Date	Time (EST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See Fig. 63)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760814	0835	0.6	B	3	270	Toronto Island			x		A	25	25
	0907	0.4	B	3	270	Niagara	x				A	30	30
	0935	0.5	B	3	270	Oakville	x				A	30	30
	1005	0.2	B	3	300	Ajax	x				A	40	40
	1445		B	2.5	150	Toronto Island	x				A	60	50
	1509		B	2.5	150	Niagara	x				A	60	60
	1535		B	2	150	Olcott	x				C	85	60
750819	1200	0.3	C	7	310	Toronto Island			x		A	50	50
	1221	1.0	C	7	310	Niagara			x		A	55	55
	1245	1.0	C	8	300	Olcott			x		A	60	55
	1340		C	9	290	40 km East of Oshawa	x				A	60	60
750827	1345	0.2	A	2	270	Toronto Island			x		A	40	40
	1400	0.2	A	2	270	Niagara	x				A	65	50
	1433		B	3	290	Olcott	x				C	90	50
	1510	0.2	B	4	310	Ajax	x				A	60	50
750828	0853	0.2	B	3	170	Toronto Island	x				A	30	40
	0917	0.5	A	3	170	Niagara	x				F	40	40
	0945	0.7	A	2.5	160	Olcott	x				A	45	40
	1015	0.2	A	2	150	Ajax	x				A	45	45
	1340	0.2	B	4	180	Toronto Island	x				E	70	60
	1357	1.2	B	4	180	Niagara	x				C	90	65
	1427	0.9	B	3.5	180	Olcott	x				C	90	65
	1455	0.2	B	3	170	Ajax	x				E	50	90
	1512	0.3	B	3	170	Oakville	x				D	110	80

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

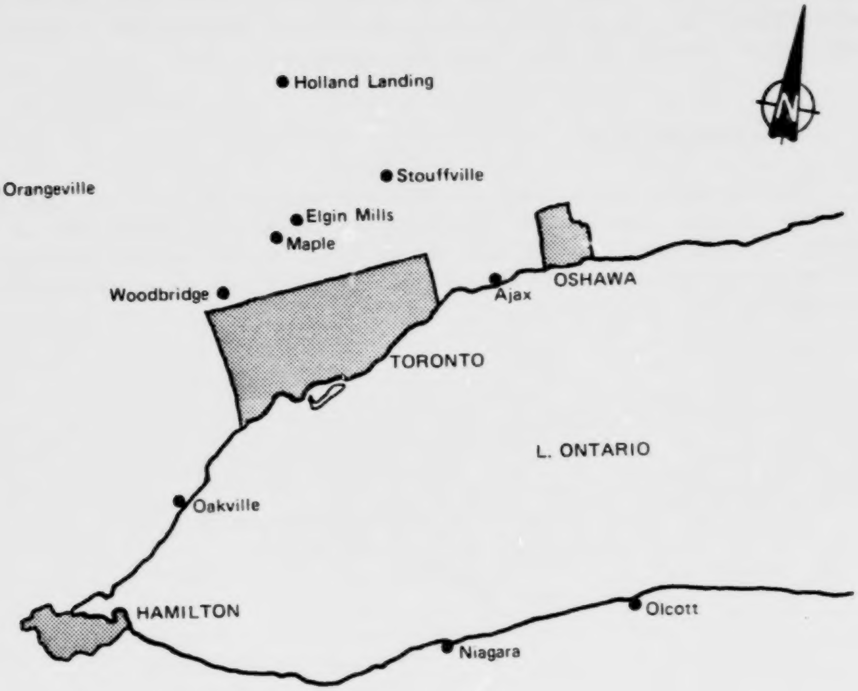


FIGURE 63 AREA IN WHICH TORONTO PROFILES WERE TAKEN

atmospheric layers above the Toronto area, or from National Weather Service analyses. Stability estimates are based on data from the same sources. It should be noted that wind observations from a single location in a lakeside environment may not adequately describe the lake breeze circulations. Therefore specifying whether a particular profile was "upwind" or "downwind" was subject to considerable uncertainty.

Lusis et al. (1976) have analyzed many of the profiles tabulated in Table 6. Their analysis suggests that some of the profiles classified as having little or no recent influence from the city might contain ozone and precursors from the preceding day that was recirculated by the lake breeze. For example, they suggested that such recirculation was responsible for the profiles observed on the morning of August 12, 1975. Their paper should be consulted for details.

6. Indianapolis

The profiles summarized in Table 7 were contained in the report of Lovelace et al. (1975). The approximate locations, relative to the center of Indianapolis, of the three areas where spiral measurements were made are given in Table 8. More details can be obtained from Lovelace et al. (1975).

Table 8

LOCATIONS OF SPIRAL MEASUREMENTS
RELATIVE TO THE CENTER OF
INDIANAPOLIS

Site	Location Relative to City Center
Indianapolis	Over center of city
West Newton	20 km southwest
Oaklandon	25 km northeast

It is evident from Table 7 that the profiles were taken in pairs, one over the city and one upwind of the city. Two pairs of observations were obtained during morning hours and three pairs during the afternoon. The wind and other meteorological data necessary for estimating stability class were reported by Lovelace, et al. (1975). One important shortcoming of these data is the relative sparsity of observations of high ozone concentration.

7. Denver

Table 9 summarizes the characteristics of the six ozone profiles measured November 21, 1973, in the vicinity of Denver, Colorado, by Blumenthal et al. (1974). Those authors gave maps showing the location

Table 7

SUMMARY OF OZONE PROFILES STUDIED FROM THE INDIANAPOLIS AREA

Date	Time (CST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
740823	1431	1.7	B	3.5	270	West Newton	x				A	75	90
	1454	0.8	B	3.5	270	Indianapolis		x			A	70	90
740825	0844	0.8	B	2.5	20	Oaklandon	x				F	15	40
	0910	0.9	B	2.5	20	Indianapolis		x			A	25	20
740912	1453	1.8	D	5	220	West Newton	x				A	20	15
	1518	1.8	D	5	220	Indianapolis		x			A	20	30
740917	1010	0.6	B	5	250	West Newton	x				B	0	10
	1036	0.7	B	5	250	Indianapolis		x			E	0	30
	1510	1.1	B	5	250	West Newton	x				D	25	20
	1531	1.1	B	5	250	Indianapolis		x			D	30	30

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

Table 9

SUMMARY OF OZONE PROFILES STUDIED FROM THE DENVER AREA

Date	Time (MST)	Mixing Depth (km msl above ground)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile (See text)	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
731121	0822	0.3				Site 3	x				B	5	40
	0915	0.2				Site 2			x		B	10	40
	0925	0.2				Site 1			x		B	10	30
	1135	0.3				Sice 3			x		D	70	75
	1234	0.1				Site 2	x				A	50	50
	1242	0.2				Site 1	x				A	50	50

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

where the ozone profiles were measured. Sites 1 and 2 are to the northeast of the Denver Civic Center at distances of about 12 and 18 km, respectively. Site 3 is about 17 km to the northwest. The determination of whether or not the sites were downwind of Denver was based on the analyses presented by Blumenthal et al. (1974). Needless to say, November is not a month conducive to photochemical activity, but these data do extend the geographical and seasonal scope of the available profile data.

8. Tampa Bay, Florida

Washington State University measured ozone concentrations at various altitudes in the vicinity of Tampa Bay during May of 1976. Some of the data collected were included in an EPA memorandum from Lonneman (1977) to J. J. Bufalini. The nature of the profiles included with that memorandum is summarized in Table 10. It is anticipated that more detailed information about these profiles and more profiles from the same study will be published at a later date. However, the limited sample in Table 10 was included for purposes of statistical analysis. These data broaden the geographical scope of the total data base.

C. Vertical Cross Sections of Ozone Concentration in the Northeastern United States

The examples of the vertical distribution of ozone given in the preceding sections have been limited to isolated vertical profiles taken at locations directly above or outside a city, either upwind, downwind, or to one side. Ludwig and Shelar (1977) analyzed data collected by four groups that participated in the Northeast Oxidant Study Environmental Monitoring and Support Laboratory, 1975; Siple et al. 1976; Spicer et al. 1976; Washington State University, 1976; Wolff et al. (1975). The large numbers of vertical profiles taken at different locations at approximately the same times allowed Ludwig and Shelar to analyze the data in the form of vertical cross sections that show the distribution of ozone concentration in a plane perpendicular to the surface. The vertical cross sections provide interesting displays of the urban plume structure. The presence of elevated ozone layers is also seen easily in this kind of display.

Vertical cross sections are similar to the ozone isopleth maps that were used to display ground-level concentration patterns in the St. Louis, Los Angeles, and Houston areas, but the plane in which the concentrations are mapped is vertical, as opposed to being the ground surface itself. In the figures presented later in this section, the line above which a cross section applies has been shown on a map of the region. The basic data were obtained from aircraft measurements above points that are marked on the maps. The vertical extent of the aircraft measurements is indicated by vertical lines on the cross section. Stable layers have been marked by stippled bars. Wind directions at

Table 10

SUMMARY OF OZONE PROFILES STUDIED FROM THE TAMPA BAY AREA

Date	Time (EST)	Mixing Depth (km msl)	Pasquill Gifford Stability Class*	Wind (Approximate)		Location of Ozone Profile	Location Relative to the City				Ozone Profile Type	Approximate Ozone Concentration (ppb)	
				Speed (m/sec)	Direction (deg)		Upwind or Side	Within the City	Downwind	Unknown		At Surface	Average in Mixed Layer
760513	0823	0.9		3	160	SW	x				F	10	20
	1229	0.9		3.5	200	SW	x				F	25	25
	1423	0.8		3.5	200	N			x		E	25	40
	2134	0.5		5	190	SW	x				A	20	25
760514	1049	1.0		7	150	SW	x				F	25	35

*A = extremely unstable; B = moderately unstable; C = slightly unstable; D = neutral

850 mb (about 1500 m) are shown by stream lines. The times (EST) of the aircraft measurements are shown on the cross sections. In many instances, analyses of the ozone concentrations observed at ground level have been used to extend the analysis of the vertical soundings down to the surface.

Figure 64 shows two cross sections based on data collected during the afternoon of August 10, 1975. The stream lines show the 850-mb winds for 1900 EST. The cross sections are based on data collected somewhat earlier, between 1545 and 1715 EST. The two cross sections show that there were layers of high ozone concentration aloft. In the

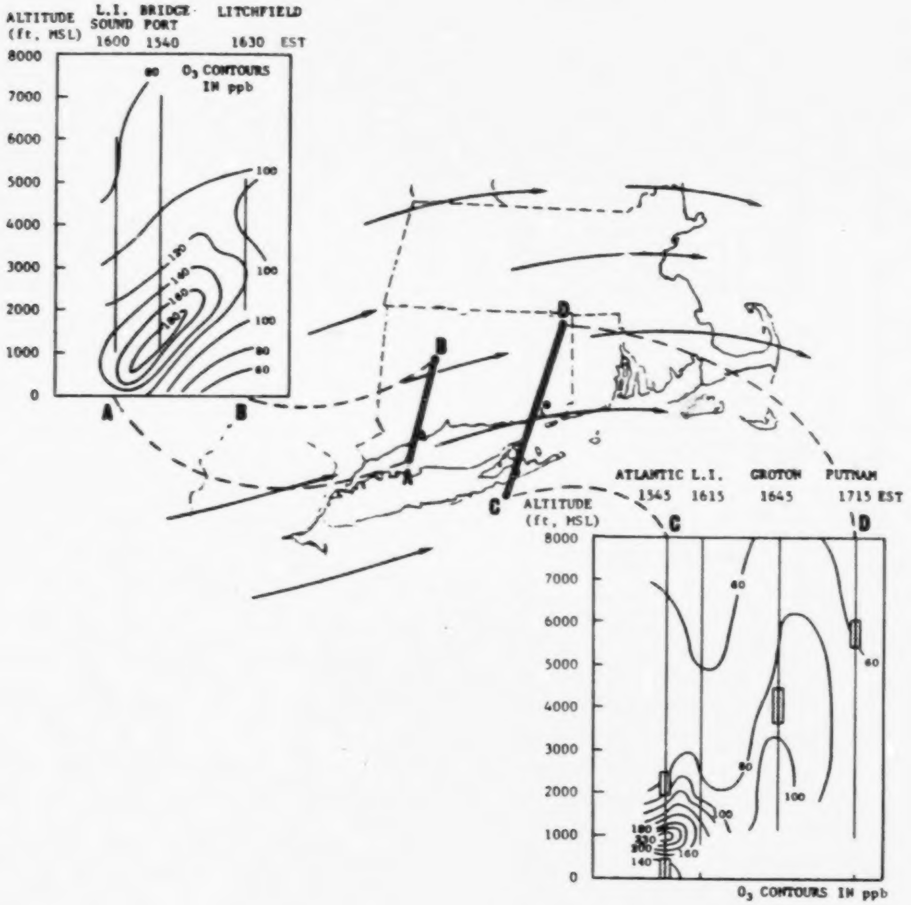


FIGURE 64 VERTICAL CROSS SECTIONS OVER CONNECTICUT 1545-1715, AUGUST 10, 1975

western cross section, concentrations exceed 180 ppb at a height of about 1300 ft (400 m) above the Connecticut coast. Farther downwind, ozone concentrations were less. The eastern cross section shows concentrations of about 125 ppb. At the southern end of this same eastern cross section, concentrations aloft exceeded 230 ppb. The southernmost vertical sounding in the eastern cross section shows that there was a stable layer at the surface, probably caused by the passage of air over the colder Atlantic waters. Within the surface-based stable layer, concentrations fell below 140 ppb, while aloft they exceeded 230 ppb. Another stable layer had a base at about 600 m (2000 ft); high ozone concentrations were confined below the upper stable layer. It is apparent that the profile at this southernmost point on the cross section is a Type E. It is also apparent from these analyses that a Type E profile can result from the urban "plume," especially when it travels over a surface that causes the lower layers to become stable, or when the air passes over an area where the surface emissions of NO deplete the ozone in the lowest layer.

Figure 65 provides another example of the elevated urban plumes. The measurements shown in this figure were made during the afternoon of August 12, 1975. At the northeastern end of this cross section, concentrations were relatively uniform in the vertical, about 60 ppb. Farther to the southwest along the cross section, the plume from Boston becomes apparent, with concentrations greater than 160 ppb at about 500 m (1650 ft). At the lower altitudes over Cape Cod Bay and the Atlantic Ocean, the concentrations were less than 80 ppb. This again appears to be a Type E profile, formed when the lowest layer of the atmosphere was stabilized by passage over a cool water surface, and the ozone that was removed at the surface could not be replaced by downward mixing of the ozone aloft. Part of the plume from New York is evident at the southwest end of the cross section shown in Figure 65. Concentrations at about 300 m (1000 ft) exceed 240 ppb, while surface concentrations are slightly less, around 200 ppb. This suggests that mixing was more pronounced in the lowest layers in this area than above the cooler water surfaces, and that this was a Type D profile.

Figure 66 shows two cross sections based on measurements during the morning of August 21, 1975. This particular date provides an example of the behavior of urban plumes when an area is under the influence of a large anticyclone (high-pressure area) to the east. Although the two cross sections shown in Figure 66 are reasonably close together in space, the line that is more to the northwest is based on data that were collected upwind of, or above, the major urban centers. Ozone concentrations over central New Jersey exceeded 80 ppb, but no values as high as 100 ppb were found. In general, concentrations were quite uniform with height but tended to decrease toward the northeast at all altitudes. The uniformity in concentration with height indicates that this was a well mixed body of air, representing "background conditions," and that the vertical profiles were Type A.

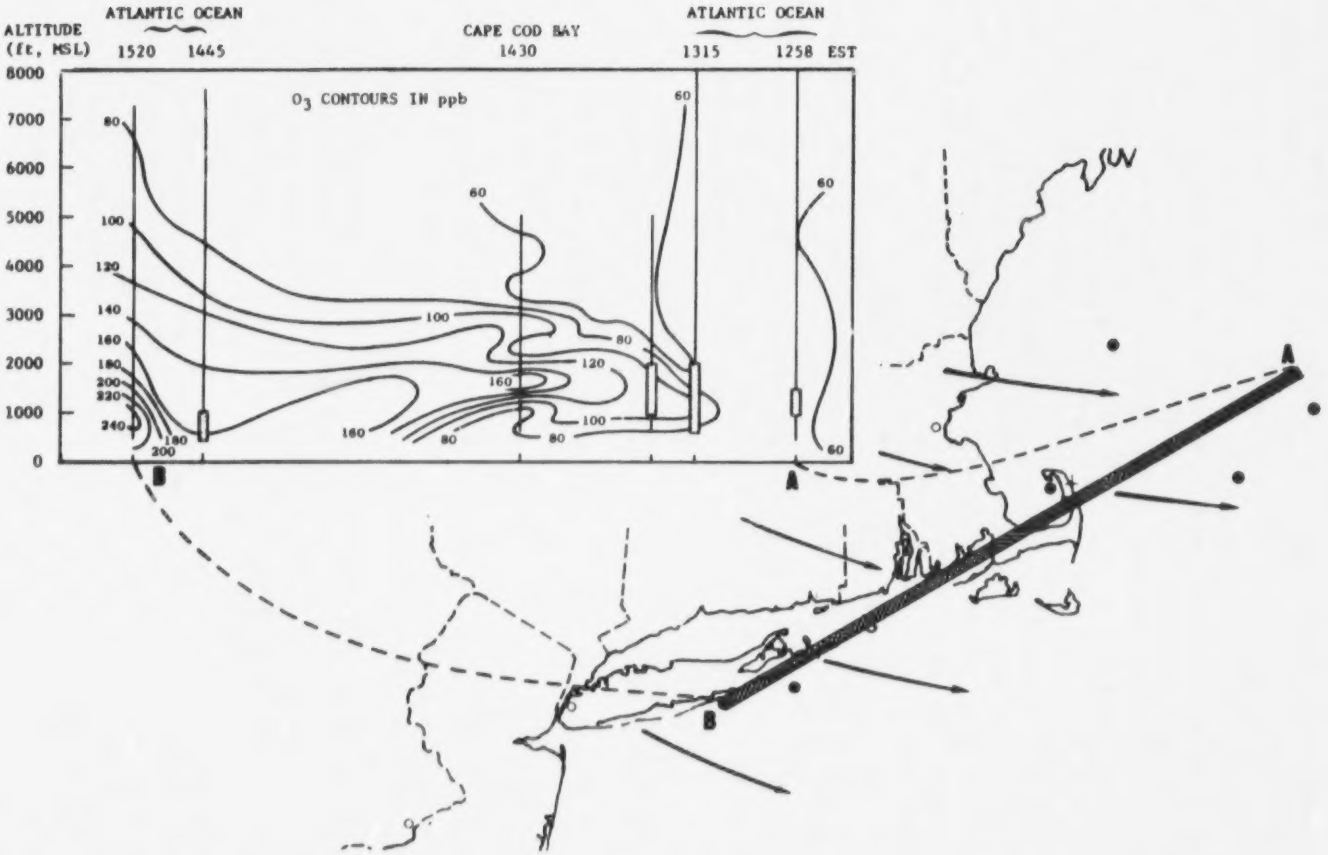


FIGURE 65 VERTICAL CROSS SECTION FROM LONG ISLAND THROUGH CAPE COD, 1258-1520, AUGUST 12, 1975

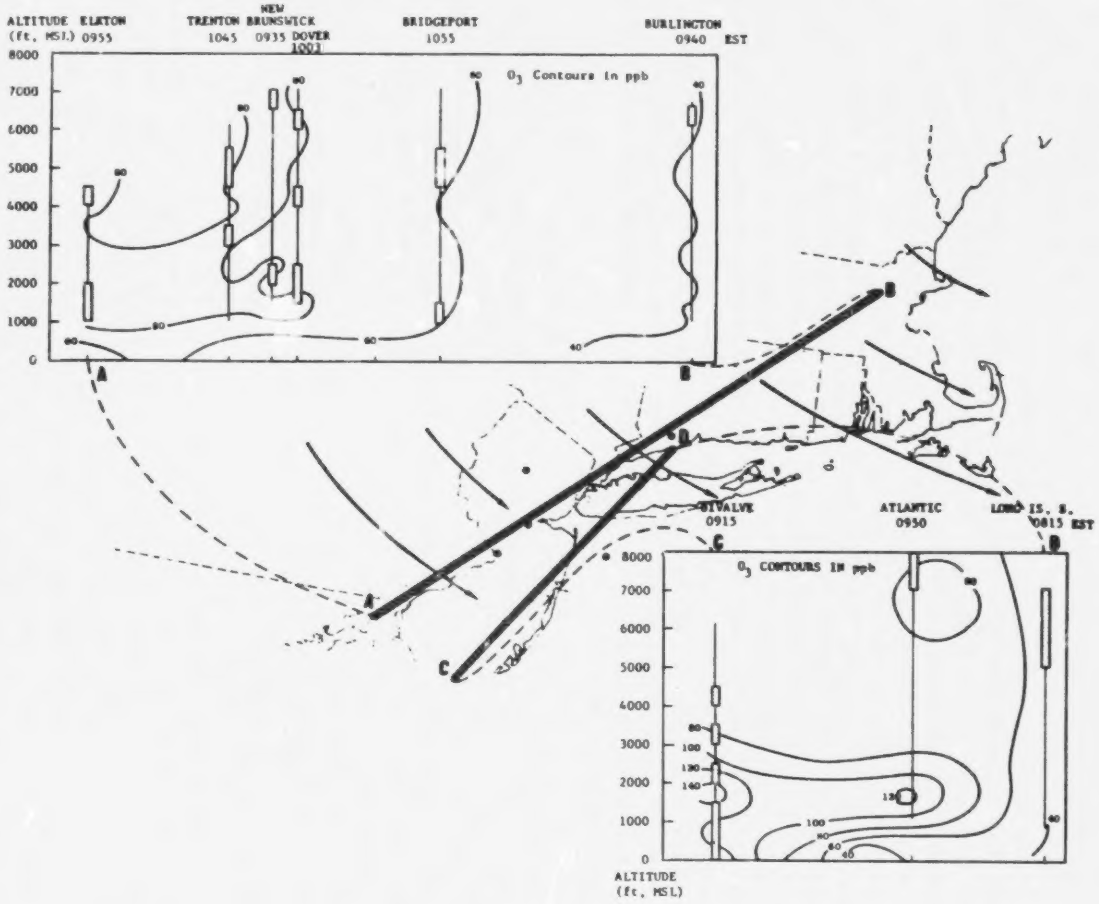


FIGURE 66 VERTICAL CROSS SECTIONS OF OZONE CONCENTRATION, 0815-1055, AUGUST 21, 1975

The other cross section in Figure 66 has a very different appearance. Ozone concentrations as great as 140 ppb were observed in a layer between 1500 and 2000 ft (450 and 600 m), even though the measurements were made in the morning before the time when one would expect maximum photochemical production of ozone. Morning 850-mb wind patterns shown in the figure suggest that the high concentrations observed over the Atlantic might have arisen from emissions in the Newark-New York area. The vertical uniformity of the low concentrations at the northeast end of this cross section, where it is close to the other cross section, gives much the same picture of "background conditions" as can be seen in the other cross section. The high concentrations that were observed at the southwest end of this cross section are more difficult to explain; the only metropolitan area lying upwind is Wilmington, Delaware, but it is also possible that these high concentrations are at the northern edge of a plume from Baltimore. That explanation would require a more southerly component to the air motion than is seen in the 850-mb wind field. However, surface weather maps show that ground-level winds were light and from the south-southeast, so it is quite possible that net transport at 2000 ft (600 m) might have been from the Baltimore area. Ludwig and Shelar (1977) attribute the lack of evidence for a plume of high ozone concentration downwind of Philadelphia to the lack of vertical profile measurements of concentration in the appropriate places, suggesting that had such measurements been made, they would have revealed evidence of Philadelphia's effects.

Figure 67, based on data collected during the midafternoon hours of August 21, 1975, displays complex patterns aloft that are difficult to interpret. Concentrations in excess of 200 ppb were observed at about 4000 ft (1200 m) over southern Connecticut. Concentrations in excess of 140 ppb were found over New Jersey, and near the eastern end of the cross section. Part of the complexity in that data arises from the rather large time span covered by the data, from 1325 to 1550 EST. Presumably, the patterns would have been somewhat more organized had the measurements been made at more nearly the same time. The most important physical reason for the complexity is probably the light wind conditions that prevailed. According to Wolff et al. (1975), the early morning winds this day were light and from north to northeast. The surface winds shifted to southwesterly during the afternoon. Wolff et al. (1976) have analyzed this day extensively and concluded that the ozone and precursor emissions from urban areas such as Philadelphia, Baltimore, and Washington had accumulated during a period of light winds that lasted from late evening on August 20 until the early morning hours the following day. Zeller (1976) believes that the plumes seen in Figure 67 may have come from Philadelphia, New York, and Hartford, having traveled to the southwest in the morning and then returned to the north later during the day. In any event, there was a complex mixture of ozone and precursors that came from several different urban areas. During the morning, the mixture was relatively uniform and showed only the effects of the most recent precursor emissions. As the day progressed, ozone was formed from the residual precursors and from the more recent emissions, which resulted in the very complex patterns seen in Figure 67. Figure 67

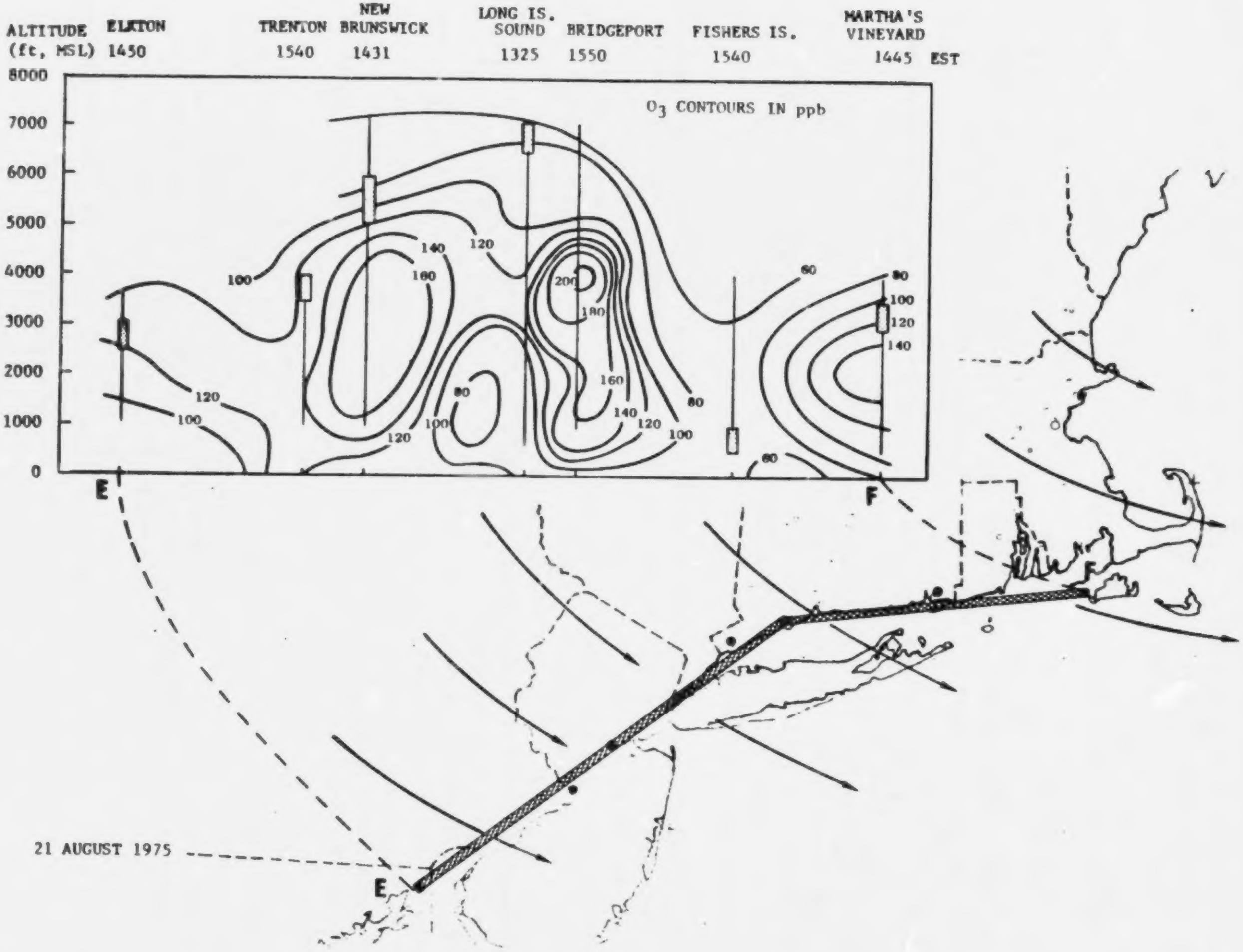


FIGURE 67 VERTICAL CROSS SECTION OF OZONE CONCENTRATION, 1325-1550 EST, AUGUST 21, 1975

shows that in a region with many closely spaced areas of precursor emission, it is not always possible to define vertical ozone profiles in terms of "upwind" or "downwind". Generally, the characteristics of each profile can still be fit into the classification scheme described here, but much of the physical significance that goes with that classification system is obscured.

D. Summary of Ozone Profile Features

1. General

Earlier sections of this report have described how the pollutant profiles can be categorized according to their shape and how the shapes relate to various physical processes operating in the atmosphere. Many examples were presented and discussed. In this section, we present some statistics to show when and where certain types of profiles are most likely to be found. The relationships between surface ozone concentrations and those aloft are also examined in terms of how they relate to the different categories of profile. The effects of stability, time of day, and location relative to the city on the surface/mixing-layer concentrations are also examined.

All comparisons are based on analysis of the complete data sample--that is, the information for all the profiles enumerated in Tables 1, 3, 4, 5, 6, 7, and 9. It should be borne in mind while interpreting the results of the analysis that there are substantial differences in the data sets for the different cities. The data sets for some cities emphasize the morning hours, for others the afternoon; different seasons are represented and the mixtures of upwind, downwind, and in-city observations change from one data set to another. Thus, the possibility exists that results appearing to represent diurnal effects or the effects of positions relative to the city might in fact have been produced by differences among the cities. However, the results obtained are consistent enough with known physical processes that the conclusions drawn are unlikely to have been substantially influenced by city-to-city differences on the data sets.

One serious shortcoming remains in the available data. Nighttime, stable atmospheric conditions are virtually unrepresented. This almost certainly means that the occurrence of profiles of Type B and Type E is more frequent than indicated by the data set. Similarly, the data set contains more examples of profiles taken in areas relatively free of recent urban influence than it does of profiles taken over the city itself or in downwind areas. This, too, is likely to bias the estimates of the relative frequency of occurrence of the different types of profile.

It must be recognized that the statistics on ozone profile classes that are presented in this section are not the product of a wholly objective process. The statistics should be useful for defining the relative frequencies found for the different types of profile under varying circumstances, but they should not be applied in an absolute sense to other areas. The classification was done with the physical factors that govern the shape of the profiles in mind. Thus, there is apt to be a bias that makes the statistics more as would be expected from physical principles than would be the case if the classifications had been made in isolation from a knowledge of the governing factors.

2. Characteristics of the Different Types of Profile

a. General

Of the 268 cases classified, 80 were judged to be Type A profiles. The next most commonly observed were Type D (68 cases) and Type F (54). Only 13 Type B and 32 Type E profiles were in the sample. This is probably a reflection of the sampling bias that exists with regard to time of day. Profiles were categorized as Type C in 21 instances. The Type C profile should probably occur downwind of an urban area, but relatively close to it, and it may well be that vertical profiles were seldom taken at the appropriate locations.

With regard to time of day, the overall sample includes only 9 cases for the hours between 1800 and 0600 local time. For the hours between 0600 and 0900, there were 58 cases, and 77 cases between 0900 and noon. During the afternoon, 74 cases were observed between noon and 1500, and 51 cases between 1500 and 1800.

By far the largest number of profiles were measured in locations judged to be relatively free of recent urban influences; 133 profiles were measured in such locations. Downwind cases numbered 51, while 67 were taken above the city. This leaves only 18 cases that could not be classified.

b. Relative Frequency During Different Times of Day

Table 11 is a contingency table showing the frequency at which different combinations of profile type and times of day were observed. The first number in each square is the number of cases having the combination of profile type and time of day represented by that square. The second number shows the percentage of the total number of cases in that row (time interval) that had the characteristics of that column (profile type). The third figure in the square shows the percentage of the total cases in that column (profile type) that occurred with the characteristics represented by that row (time interval). Finally, the last number in the square shows the percentage of the total cases that had the combination of characteristics represented by the square.

For example, consider the second row and second column of Table 11. In this instance, the sample contained 12 Type A profiles that occurred

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Table 11

FREQUENCY OF OCCURRENCE OF DIFFERENT PROFILE TYPES
AT DIFFERENT TIMES OF DAY

TIME INTERVAL — local standard time

```
              COUNT   I
              ROW PCT I                           PROFILE TYPE                                 ROW
              COL PCT I                                                                       TOTAL
              TOT PCT I UNCERTAIN I A        I B        I C        I D        I E        I F        I
              --------I----------I----------I----------I----------I----------I----------I----------I
                 1.   I       0  I       0  I       2  I       0  I       0  I       2  I       0  I      4
BEFORE 600            I       0  I       0  I    50.0  I       0  I       0  I    50.0  I       0  I    1.5
                      I       0  I       0  I    15.4  I       0  I       0  I     6.3  I       0  I
                      I       0  I       0  I      .7  I       0  I       0  I      .7  I       0  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 2.   I       0  I      12  I       6  I       0  I       2  I      10  I      28  I     58
600-900               I       0  I    20.7  I    10.3  I       0  I     3.4  I    17.2  I    48.3  I   21.6
                      I       0  I    15.0  I    46.2  I       0  I     2.9  I    31.3  I    51.9  I
                      I       0  I     4.5  I     2.2  I       0  I      .7  I     3.7  I    10.4  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 3.   I       0  I      35  I       4  I       4  I      10  I       9  I      15  I     77
900-1200              I       0  I    45.5  I     5.2  I     5.2  I    13.0  I    11.7  I    19.5  I   28.6
                      I       0  I    43.8  I    30.8  I    19.0  I    14.7  I    28.1  I    27.8  I
                      I       0  I    13.0  I     1.5  I     1.5  I     3.7  I     3.3  I     5.6  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 4.   I       0  I      25  I       0  I       9  I      27  I       8  I       5  I     74
1200-1500             I       0  I    33.8  I       0  I    12.2  I    36.5  I    10.8  I     6.8  I   27.5
                      I       0  I    31.3  I       0  I    42.9  I    39.7  I    25.0  I     9.3  I
                      I       0  I     9.3  I       0  I     3.3  I    10.0  I     3.0  I     1.9  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 5.   I       1  I       7  I       0  I       7  I      27  I       3  I       6  I     51
1500-1800             I     2.0  I    13.7  I       0  I    13.7  I    52.9  I     5.9  I    11.8  I   19.0
                      I   100.0  I     8.8  I       0  I    33.3  I    39.7  I     9.4  I    11.1  I
                      I      .4  I     2.6  I       0  I     2.6  I    10.0  I     1.1  I     2.2  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 6.   I       0  I       0  I       0  I       1  I       2  I       0  I       0  I      3
1800-2100             I       0  I       0  I       0  I    33.3  I    66[illegible]  I       0  I       0  I    1.1
                      I       0  I       0  I       0  I     4.8  I     2.9  I       0  I       0  I
                      I       0  I       0  I       0  I      .4  I      .7  I       0  I       0  I
                     -I----------I----------I----------I----------I----------I----------I----------I
                 7.   I       0  I       1  I       1  I       0  I       0  I       0  I       0  I      2
2100-2400             I       0  I    50.0  I    50.0  I       0  I       0  I       0  I       0  I     .7
                      I       0  I     1.2  I     7.7  I       0  I       0  I       0  I       0  I
                      I       0  I      .4  I      .4  I       0  I       0  I       0  I       0  I
                     -I----------I----------I----------I----------I----------I----------I----------I
               COLUMN         1         80         13         21         68         32         54       269
                TOTAL        .4       29.7        4.8        7.8       25.3       11.9       20.1     100.0
```

between 0600 and 0900. This represented 20.7 percent of all the data collected between 0600 and 0900 and 15.0 percent of all the Type A profiles. Finally, 4.5 percent of all the observations were taken between 0600 and 0900 and were of Type A. The first column of the table shows that the sample includes one case where the ozone profile was not classified as to type.

Examination of the columns in Table 11 shows that the times at which the different profile types are observed differed considerably from one to another. For example, 83.9 percent of the Type A profiles were observed between 0900 and 1800 local time. By contrast, only 30.8 percent of the Type B profiles were observed during this time period, and all of those were before noon. Well over 90 percent of the C and D profiles were also observed during the daytime hours between 0900 and 1800. Type F profiles, which represent those cases with ozone layers isolated aloft, were far more common during the forenoon, when nearly 80 percent of the cases occurred, than during the afternoon, when the ozone isolated aloft was likely to be mixed more thoroughly through the mixing layer. Type E profiles were distributed reasonably evenly through the day; those that occurred during the late forenoon and afternoon are probably the result of instances when the strong vertical gradients of ozone concentration near the surface, associated with this type of profile, were caused by the destruction of ozone by urban NO emissions. The occurrences of Type E profiles at other hours of the day are more likely to have been caused by a nocturnal, surface-based stable layer that isolated ozone aloft, preventing surface destruction.

Table 11 shows the expected differences in diurnal distribution of the different kinds of ozone profile. Application of the chi-square test (Nie et al., 1975) to these data indicates that the differences in the diurnal distributions are highly significant. The chances of obtaining results like those shown in Table 11 are less than 0.01 percent if there are no differences in the frequencies at which the profile types occur at different times of day.

c. Relative Frequencies at Different Locations Relative to the Urban Areas

Table 12 shows the relative frequency at which the different profile types occurred in different locations relative to the city. The key to the entries is the same as for Table 11. The entries in the second column of the first row shows that there were 51 observations of Type A profiles upwind or to one side of urban areas; this represented 38.3 percent of all observations made upwind or to one side of the city and 63.8 percent of all Type A profile observations.

Table 12 shows the expected relationships. For example, Type A profiles were observed over 35 percent of the time in locations relatively uninfluenced by the city, but only around 20 percent of the time in areas above or downwind of the city. Type D profiles were found in only 18 percent of the observations where the profile was believed to be uninfluenced by the city, but in over 37 percent of those instances downwind of the city. Similarly, the Type C profile represents a much larger proportion of downwind profiles than of profiles uninfluenced by the city.

The differences in the frequency at which the different profile types occurred in different locations relative to the city are significant, according to the chi-square test (Nie, 1975). The probability of observing these differences would be less than 1 percent if there were no differences from place to place.

3. Relationship Between Surface Ozone Concentrations and Those in the Mixed Layer

a. General

One of the major purposes for analyzing the ozone profiles is to be able to relate surface ozone measurements to those aloft. In this section, surface ozone concentrations are compared with those aloft to see how they vary with ozone profile type, time of day, atmospheric stability, location relative to the city, and, finally, the concentration of the ozone at the surface itself.

Some difficulties arise trying to define average ozone concentrations "aloft." Some upper height limit must be established before it is possible to estimate the average ozone concentration aloft. The top of the mixing layer has physical significance and measurements usually were taken at least to that height or high enough so that one could reasonably infer the concentrations that were likely between the top of the measured profile and the top of the mixing layer. Nevertheless, the use of the mixing depth to define the region in which average concentrations should be estimated presents some problems, especially when the lowest layers are stable or mixing is otherwise confined to a very shallow layer. In such cases, much higher concentrations were often isolated above the layer for which the average concentration was determined. Thus, for profiles of Types E or F (Figure 4), the concentrations deemed to be the average for the mixing layer may be substantially less than the concentrations just above the top of the layer. This should be borne in mind when interpreting the results, especially for Types B, E, and F.

The estimation of the depth of the mixed layer was to some extent subjective. In most cases there was very little ambiguity. Frequently, the top of the mixed layer would be marked by the bottom of an inversion in the lapse rate, the top of the moist layer, and the top of a layer polluted with aerosols (Bscat) and ozone. Above the layer, the air would be warmer, drier, and cleaner. Examples of such unambiguous cases can be seen in Figure 57. For those cases with surface cooling, at night or during the late afternoon, the top of the mixed layer was judged to coincide with the top of the inversion or the height at which the ozone

Table 12

FREQUENCY OF OCCURRENCE OF DIFFERENT PROFILE TYPES
AT DIFFERENT LOCATIONS RELATIVE TO THE CITY

```
LOCATION RELATIVE TO THE CITY

                CCUNT    I
                ROW PCT  I                              PROFILE TYPE                             ROW
                CUL FCT  I                                                                        TOTAL
                TOT PCT  I UNCERTAIN IA        IE        IC        ID        IE        IF        I
                ---------I----------I---------I---------I---------I---------I---------I---------I
                         I       1  I     51  I      5  I      9  I     24  I     19  I     24  I   133
  UPWIND OR              I      .8  I   38.3  I    3.8  I    6.8  I   18.0  I   14.3  I   18.0  I   49.4
  TO ONE SIDE            I   100.0  I   63.8  I   38.5  I   42.9  I   35.3  I   59.4  I   44.4  I
                         I      .4  I   19.0  I    1.9  I    3.3  I    8.9  I    7.1  I    8.9  I
                        -I----------I---------I---------I---------I---------I---------I---------I
  ABOVE                  I       0  I     14  I      4  I      1  I     19  I      9  I     20  I    67
  CITY                   I       0  I   20.9  I    6.0  I    1.5  I   28.4  I   13.4  I   29.9  I   24.9
                         I       0  I   17.5  I   30.8  I    4.8  I   27.9  I   28.1  I   37.0  I
                         I       0  I    5.2  I    1.5  I     .4  I    7.1  I    3.3  I    7.4  I
                        -I----------I---------I---------I---------I---------I---------I---------I
                         I       0  I      9  I      4  I      9  I     19  I      4  I      6  I    51
  DOWNWIND               I       0  I   17.6  I    7.8  I   17.6  I   37.3  I    7.8  I   11.8  I   19.0
                         I       0  I   11.2  I   30.8  I   42.9  I   27.9  I   12.5  I   11.1  I
                         I       0  I    3.3  I    1.5  I    3.3  I    7.1  I    1.5  I    2.2  I
                        -I----------I---------I---------I---------I---------I---------I---------I
                         I       0  I      6  I      0  I      2  I      6  I      0  I      4  I    18
  UNCERTAIN              I       0  I   33.3  I      0  I   11.1  I   33.3  I      0  I   22.2  I    6.7
                         I       0  I    7.5  I      0  I    9.5  I    8.9  I      0  I    7.4  I
                         I       0  I    2.2  I      0  I     .7  I    2.2  I      0  I    1.5  I
                        -I----------I---------I---------I---------I---------I---------I---------I
  COLUMN                         1        80        13        21        68        32        54      269
   TOTAL                        .4      29.7       4.8       7.8      25.3      11.9      20.1    100.0
```

concentrations cease to increase rapidly with height. The rationale for this choice is that the effects of the surface, on cooling and ozone destruction, have not penetrated to higher altitudes. Hence these heights mark the uppermost points where the air has been influenced appreciably by the surface through mixing. In many cases, the choice of the depths of the mixing layer was quite ambiguous and was based solely on the author's subjective judgment as to what mixing height would be most consistent with the observed profiles of temperature, humidity (dew point), aerosol concentration (Bscat), ozone concentration, and, where available, lidar or sodar records.

b. Differences Among Profile Types

Figure 68 shows the frequency distribution of the ratio of surface concentration to the average within the mixed layer, for each of the six different profile types. The numerals at the end of each bar indicate the number of instances when the ratio fell within the interval defined below the bar. More than half the Type A profiles had ratios between 0.8 and 1; more than 80 percent were between 0.8 and 1.2. By contrast, none of the eight Type B profiles had a ratio greater than 0.6. As is to be expected, Type C profiles are the only ones with an appreciable skew toward values of the ratio greater than 1. The frequency distribution of the ratio of surface to mixing-layer concentrations of ozone for Type D profiles is quite similar to that for Type A profiles. This is not surprising because the two types of profiles are quite similar in shape within the mixed layer; their differences are at altitudes above the mixed layer. This is also true of Type F profiles, and the histograms in Figure 68 are consistent with this fact. Similarly, Type E profiles resemble Type B profiles within the mixed layer, although they differ substantially above it. The histogram of the ratios for the Type E profiles is skewed toward smaller values, as is the histogram for the Type B profile, although not so pronouncedly.

The type of display shown in Figure 68 can also be used with the difference between the average mixed-layer concentration and the surface concentration. Figure 69 shows the distribution of the differences (mixed-layer concentration minus surface concentration). The three types of profile characterized by relatively uniform distribution of ozone within the mixed layer (A, D, F) all show the expected clustering of difference values around zero. Types B and E show a preponderance of positive differences, indicating that the average concentration within the mixing layer was greater than at the surface. Finally, Type C profiles show a bias toward negative differences, indicating that surface concentrations were higher than those aloft.

Table 13 presents some of the same information contained in Figures 68 and 69, but in a different way. This table gives the average ratio and the average difference values for each of the six profile types. It is obvious from Table 13 and from Figures 68 and 69 that the surface

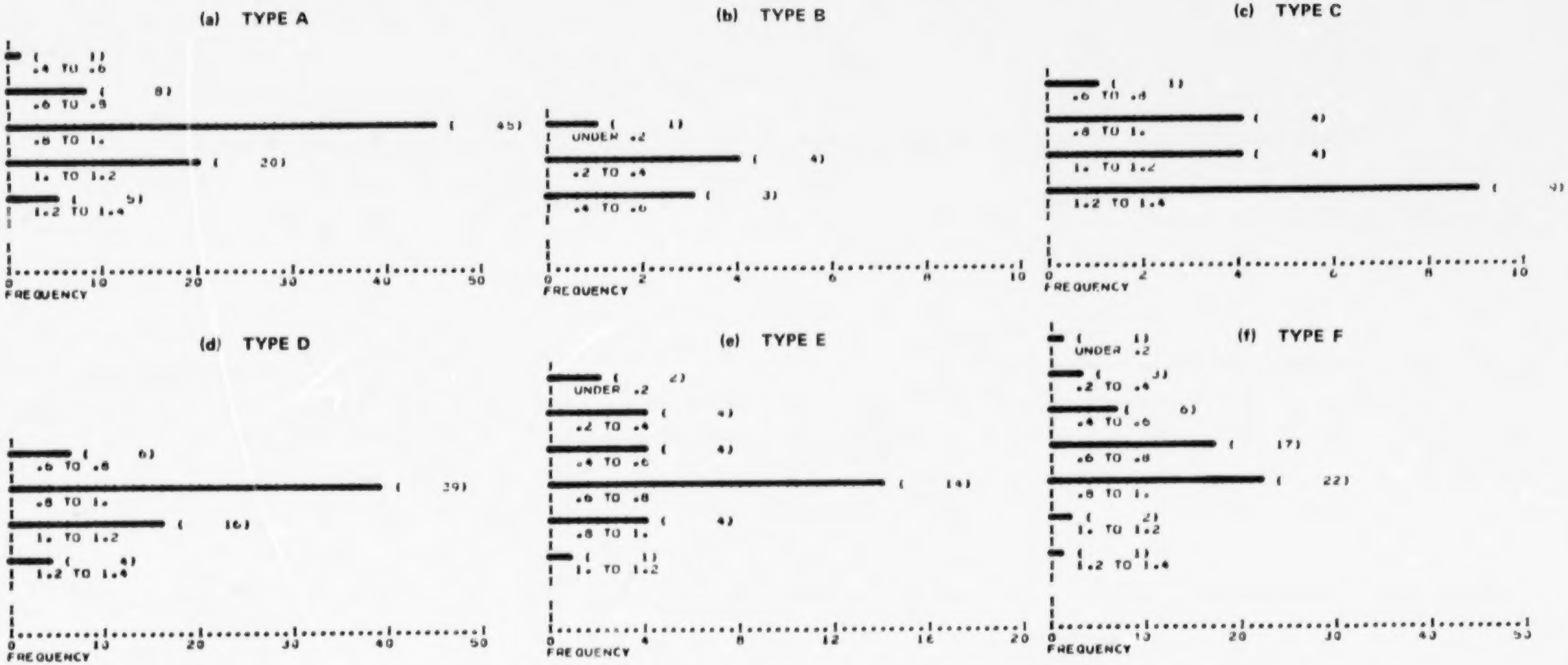

FIGURE 68 HISTOGRAMS OF THE RATIO OF SURFACE OZONE CONCENTRATION TO THE AVERAGE CONCENTRATION IN THE MIXING LAYER

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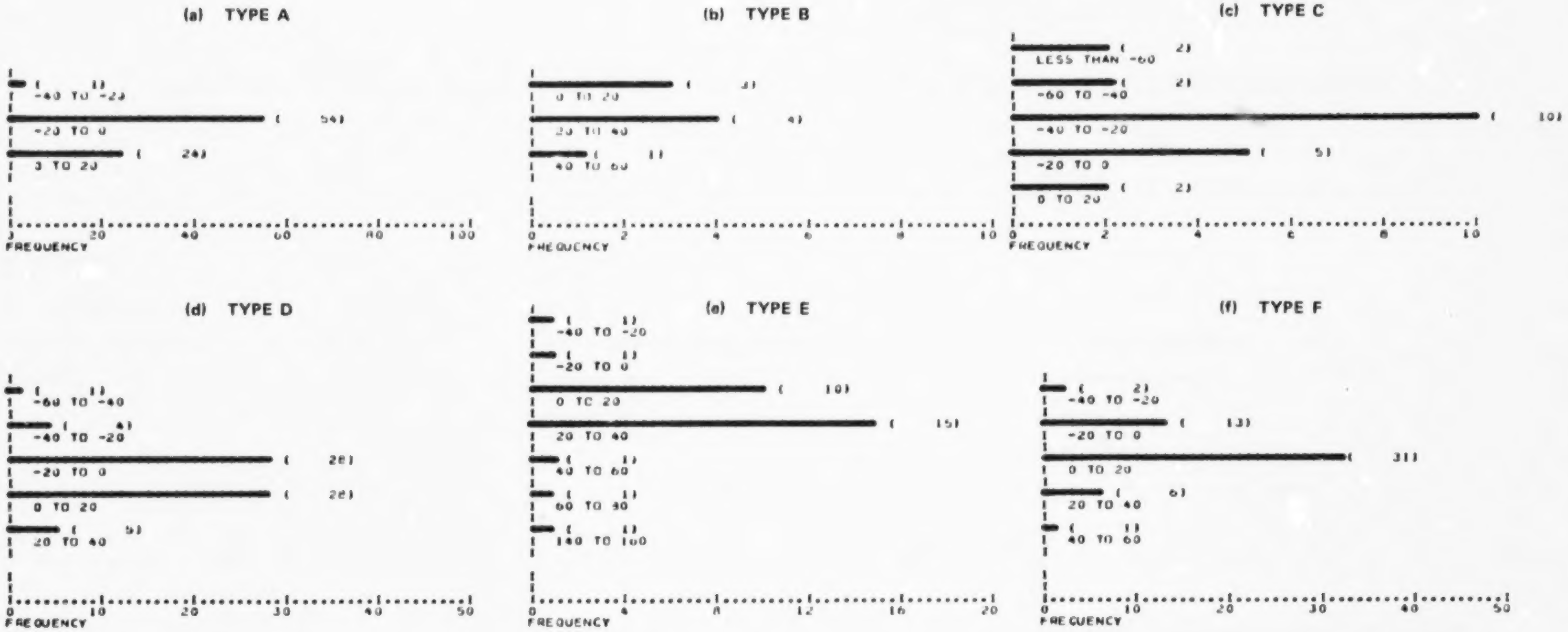


FIGURE 69 HISTOGRAMS OF THE DIFFERENCE BETWEEN AVERAGE CONCENTRATIONS OF MIXING-LAYER OZONE AND SURFACE OZONE

Table 13

AVERAGE DIFFERENCES AND RATIOS BETWEEN OZONE
CONCENTRATIONS AT THE SURFACE AND ALOFT,
FOR DIFFERENT PROFILE TYPES

Profile Type	No. of Cases	Average Difference, Mixed Layer Minus Surface Ozone (ppb)	Average Ratio (surface concentration/ mixed-layer concentration)
A	79	-0.19	1.00
B	8	27.50	0.38
C	21	-21.19	1.23
D	66	2.42	0.99
E	30	28.33	0.65
F	53	9.91	0.79

concentration is a good measure of the concentration within the mixed layer when Type A or Type D profiles are present. This will be discussed in greater detail later.

c. Different Times of Day

As already shown, there are significant differences in the frequencies at which the different profile types occur for different times of day. Also, the preceding section has shown that the differences between between surface ozone concentration and the average concentration within the mixed layer, expected to be associated with each of the different ozone profile types, do, in fact, occur. It is therefore reasonable to expect diurnal changes in the ratios and differences between surface and mixed-layer concentration. Figure 70 shows the frequency distributions of the differences and ratios for four different time periods. The figure shows that, as expected, surface concentrations are invariably less than those aloft before 0900. Throughout the day, the most common ratio of surface to mixed-layer concentration lies between 0.8 and 1, but as the day wears on, the relative frequency of surface concentrations greater than those aloft increases. According to the chi-square test (Nie et al., 1970), the diurnal

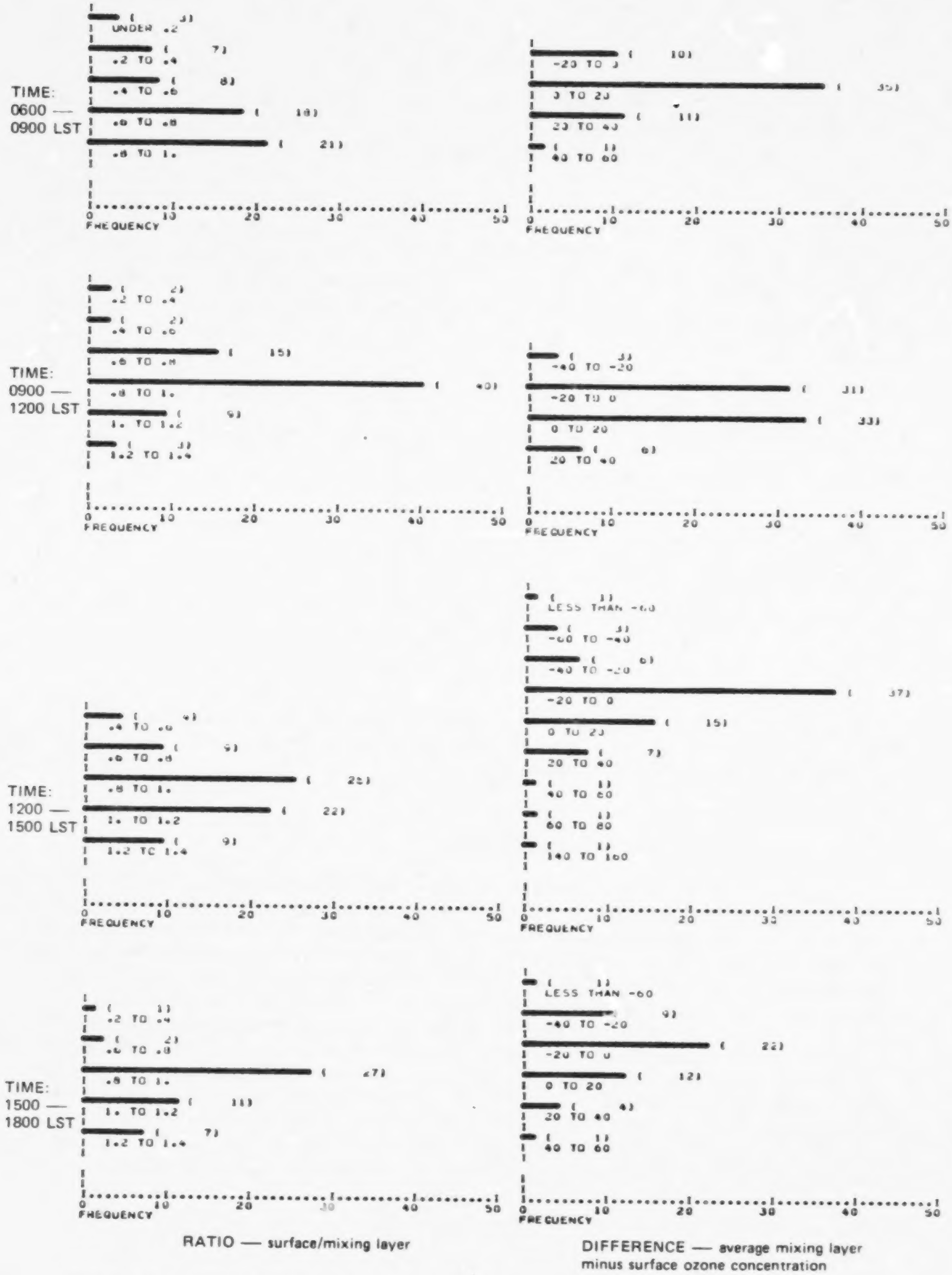


FIGURE 70 HISTOGRAMS OF RATIOS AND DIFFERENCES BETWEEN CONCENTRATIONS OF OZONE AT THE SURFACE AND IN THE MIXING LAYER, FOR DIFFERENT TIMES OF DAY

Table 14 summarizes the average difference and ratio between surface and mixed-layer ozone concentrations for different periods of the day. The trend toward greater uniformity in the vertical during the afternoon is apparent. During the morning hours, from 0600 to 0900, the surface ozone concentration is only slightly more than two-thirds the value of the mixed layer, in the mean. By afternoon, virtual uniformity is found, on average.

d. For Different Stability Classes

It should be apparent from much of the discussion to this point that the vigor of atmospheric mixing plays a large part in determining the nature of the ozone profile in the vertical. Thus we might expect to find the most unstable atmospheric conditions associated with the most nearly uniform vertical distributions of ozone. Figure 71 gives strong indications that this is true. For those measurements taken during extremely unstable conditions (A stability), the ratios of surface to mixing-layer ozone concentrations cluster around 1 and the differences between mixed-layer and surface concentrations cluster around zero. Stability increases toward Class D (neutral stability) and so does the frequency of ratios much greater and much smaller than 1. Large negative and larger positive differences also are more common under the more nearly stable conditions. The differences among the distributions of the ratios (when those cases are included that could not be classified) are significant at better than the 1-percent level. The differences among the distributions of mixing-layer and surface ozone concentrations could be due to chance, being significant only at about the 12-percent level.

Table 15 shows the averages and the standard deviations for the differences and ratio, stratified according to the stability that prevailed when the measurements were made. The ratio of surface to mixed-layer concentration varies with stability class, but the standard deviation shows a monotonic increase from the most unstable (A) to neutral (D) conditions. Similar, but much less pronounced, tendencies are evident in the difference tabulations.

e. For Different Locations Relative to the City

Although the ratios and differences discussed in preceding sections might be expected to differ from one location to another (relative to a city), it turns out that the differences are not very pronounced. For the ratio of surface ozone concentration to concentration aloft, the differences among the frequency distributions upwind, downwind, and over the city are totally insignificant. The distributions of differences between ozone concentration aloft and that at the surface have significant changes from one location to another, but only at the 10-percent level. Table 16 shows the average ratios and average differences, and it can be seen that the surface ozone concentrations tend to be about 90

Table 14

AVERAGE DIFFERENCES AND RATIOS BETWEEN OZONE CONCENTRATIONS AT THE SURFACE AND ALOFT, FOR DIFFERENT TIMES OF DAY

Time of Day (LST)	No. of Cases	Average Difference, Mixed Layer Minus Surface Ozone (ppb)	Average Ratio (surface concentration/ mixed-layer concentration)
0600-0900	57	13.6	0.69
0900-1200	73	4.7	0.92
1200-1500	72	1.9	1.02
1500-1800	49	-0.4	1.02

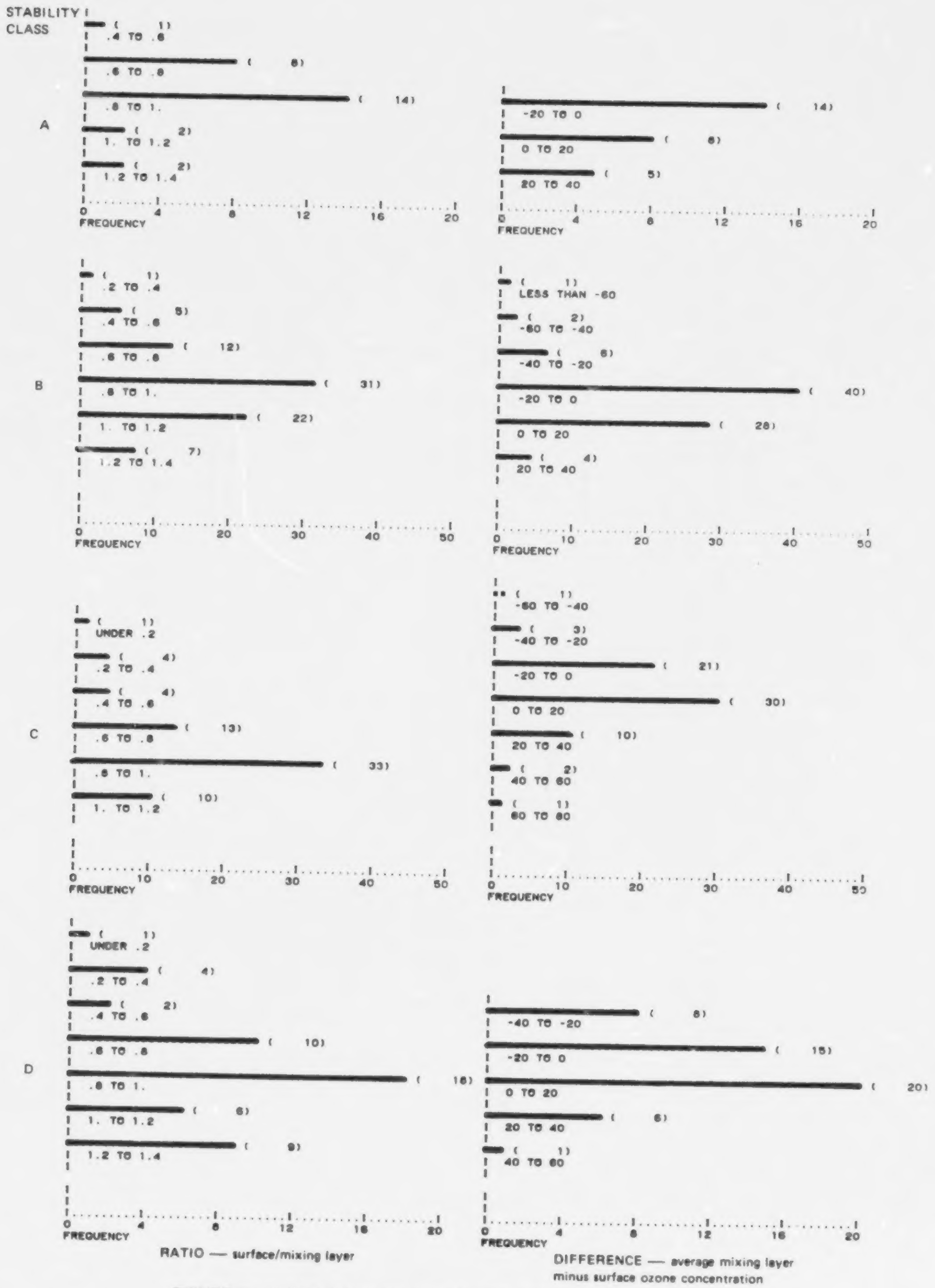


FIGURE 71 HISTOGRAMS OF RATIOS AND DIFFERENCES BETWEEN SURFACE AND MIXING-LAYER OZONE CONCENTRATIONS FOR DIFFERENT ATMOSPHERIC STABILITY CLASSES

Table 15

AVERAGES AND STANDARD DEVIATIONS FOR THE DIFFERENCES AND RATIOS BETWEEN OZONE CONCENTRATIONS AT THE SURFACE AND ALOFT, FOR DIFFERENT STABILITY CLASSES

Stability Class*	No. of Cases	Difference, Mixed Layer Minus Surface (ppb)		Ratio (surface concentration/ mixed-layer concentration)	
		Average	Standard Deviation	Average	Standard Deviation
A	27	6.5	12.5	0.92	0.18
B	81	-1.1	16.0	0.99	0.24
C	68	10.1	19.4	0.86	0.25
D	50	3.5	16.5	0.90	0.31

*A = extremely unstable; B = moderately unstable; C = slightly unstable; and D = neutral.

Table 16

AVERAGE DIFFERENCES AND RATIOS BETWEEN OZONE CONCENTRATIONS AT THE SURFACE AND ALOFT, FOR DIFFERENT LOCATIONS RELATIVE TO THE CITY

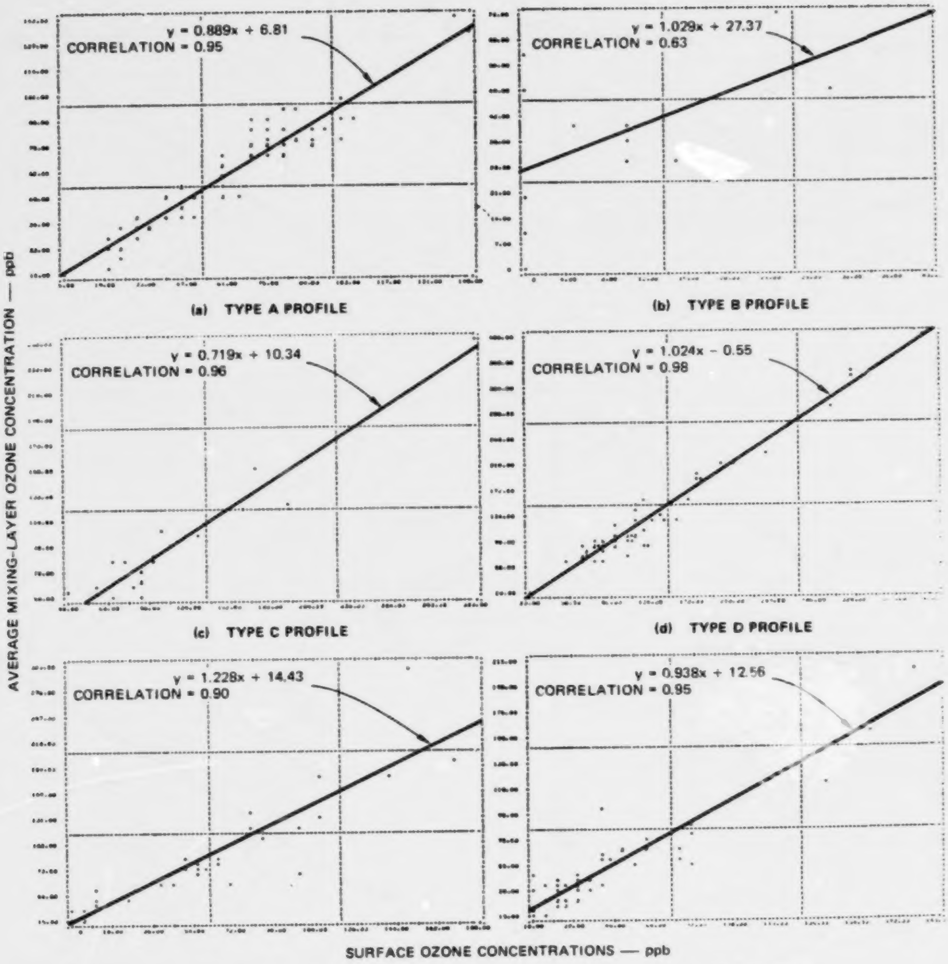
Location Relative to City	No. of Cases	Average Difference, Mixed Layer Minus Surface Concentration (ppb)	Average Ratio (surface concentration/ mixed-layer concentration)
Upwind or to one side	130	1.9	0.94
Above city	60	13.6	0.87
Downwind of city	49	5.1	0.87

percent of those in the mixed layer, regardless of location relative to the city. However, on average, the surface ozone concentration in the city is more than 13 ppb less than that averaged through the mixing layer. Outside the city, upwind or downwind, the surface ozone concentrations much more nearly approximate those averaged through the mixing layer. If the ratios remain about the same, but important changes occur in the difference, this suggests that the absolute values must be moving more or less in concert with the differences. This, in turn, suggests that the average concentrations above the city are greater than those outside it. For this sample, that is true, but it has little physical significance, because it simply reflects the dominance of Los Angeles observations in the subset of observations taken above a city. Very few Los Angeles observations were classified as being other than above the city.

f. Relations Between Surface Concentrations and Those Aloft for Different Profile Types

Figure 72 presents scattergrams of surface ozone concentration versus the average through the mixing layer, for each of the six different types of profile. The least-square fit linear regression lines and the linear correlation coefficients are also shown. If more than one case had the same combination of surface and mixing-layer concentrations, then a numeral was plotted to denote the number of cases represented by the point. As is to be expected, Figure 72 shows that mixing-layer ozone concentrations are highly correlated with surface ozone concentrations for those profiles classified as either Type A or Type D. Also as expected, the slopes of the regression lines are near unity, with small values for the intercept. The correlation and the slope of the regression line should be as they are because the profiles were classified "A" or "D" when the surface and mixing layer concentrations were about the same. It is important to note that such conditions were not at all unusual.

Although the Type C profiles have high correlations between concentrations of surface and mixing-layer ozone, the slope of the regression line is not near 1. Type F profiles exhibit good correlation between surface and mixing-layer concentrations. The slope of the regression line is near unity but its intercept is fairly large. The remaining two types of profile, Types B and E, do not show as high a correlation between surface concentrations and those averaged through the mixing layer as do the other categories, although the relationship in the case of Type E profiles is still sufficiently strong (correlation coefficient = 0.9) to be quite useful.



(a) TYPE A PROFILE

(b) TYPE B PROFILE

(c) TYPE C PROFILE

(d) TYPE D PROFILE

(e) TYPE E PROFILE

(f) TYPE F PROFILE

FIGURE 72 SCATTERGRAMS OF MIXED-LAYER AND SURFACE OZONE CONCENTRATIONS FOR THE SIX TYPES OF VERTICAL PROFILE

Figure 73(a) shows a scattergram of surface ozone concentration versus that averaged through the mixing layer for the combined subsets of data for profiles Type A and D. Obviously, if one could identify those situations where the vertical profile of ozone fell in one of these two categories, it would then be quite legitimate to infer that the ozone concentration averaged through the mixing layer was essentially the same as that observed at the surface. The regression line

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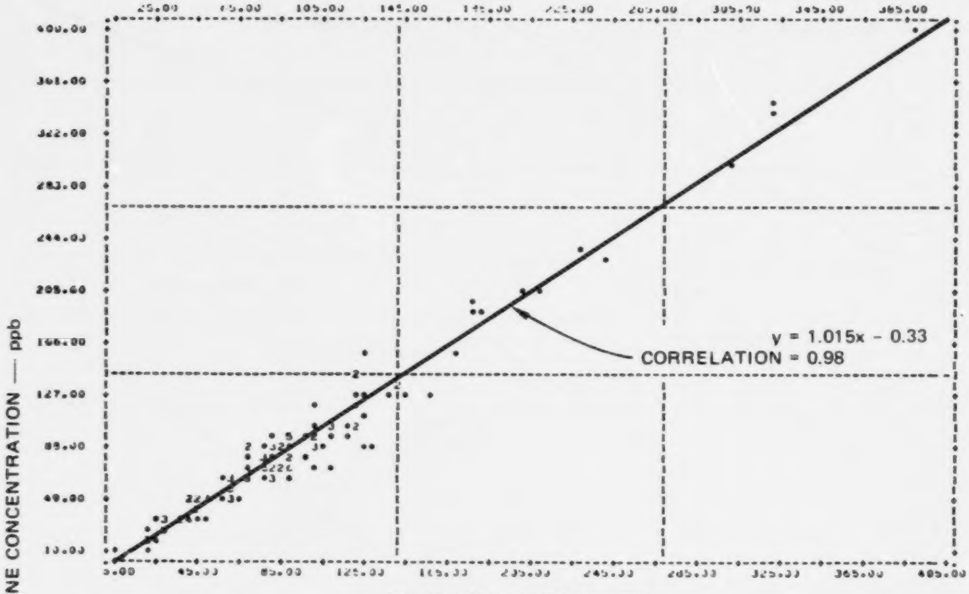
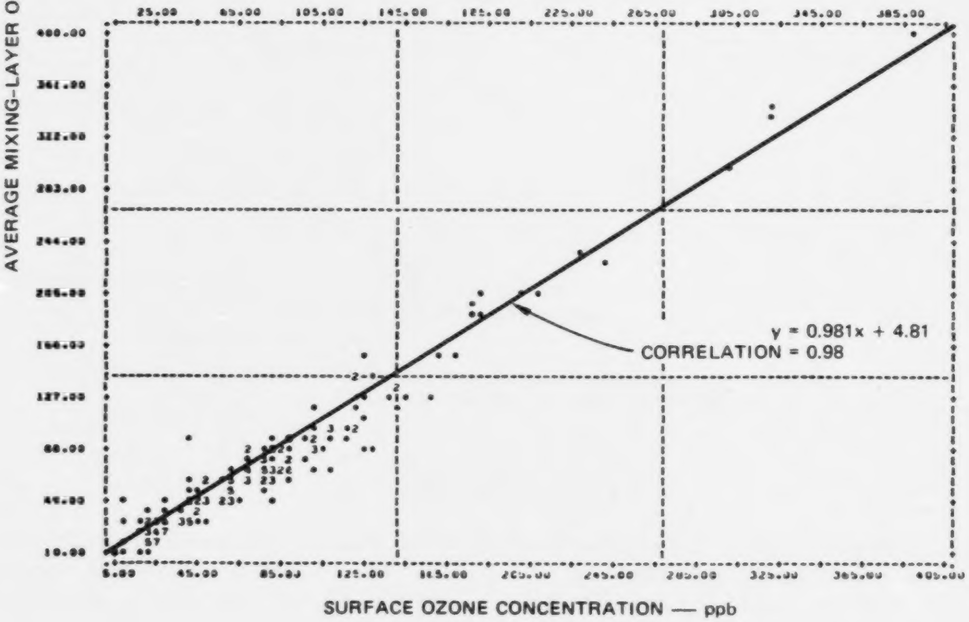


(a) PROFILE TYPES A AND D



(b) PROFILE TYPES A, D, AND F

FIGURE 73 SCATTERGRAMS OF AVERAGE MIXING-LAYER OZONE CONCENTRATIONS VERSUS SURFACE CONCENTRATIONS FOR PROFILE TYPES ASSOCIATED WITH A WELL-MIXED SURFACE LAYER

shown in the figure has a standard error estimate for the averaged mixing-layer ozone concentration of only about 11.4 ppb. It is important to note that the predictive abilities of the regression line are not limited to those cases where the ozone concentrations were low. It is obvious from Figure 73(a) that the high concentration values are also well defined by the regression line.

Profile Types A and D are associated with an atmosphere that is well mixed in the layers near the surface. Profile Type F is also associated with strong mixing in the low layers, but with the difference that the mixing has not penetrated vertically to altitudes as high as those to which earlier pollution has been mixed. Figure 73(b) shows that the inclusion of Type F profiles in the data set causes very little change in the regression line or the correlation. Thus, it is apparent that surface ozone concentrations measured under Type F conditions are representative of values through the mixing layer, but it should be remembered that this representativeness is limited to the current mixing-layer depth and that there will be higher ozone concentrations farther aloft, which are likely to be mixed downward later.

The results shown in Figure 73 would be extremely useful if it were possible to identify those times and places where one could confidently expect to find profiles of Types A and D, or even Types A, D, and F. Table 11 shows that the odds of encountering such profiles are improved considerably when the search is limited to daylight hours after 0900 local time. Between 0900 and noon, 58.5 percent of the cases are Types A or D and 78 percent are Types A, D, or F. Between noon and 1500, 73.3 percent are Types A or D, and 80.1 percent are observed to be A, D, or F.

Types B and E occur when surface destruction is not offset by vertical mixing. This can happen either when there is a strong stable layer at the surface or when surface destruction is very strong. For daytime hours after 0900, the presence of a strong stable layer will generally be unlikely, particularly on days sunny enough to be photochemically active. For the daytime hours, Types B and E will probably be associated with the strong destruction of ozone by NO that occurs in the city. Therefore, if only profiles taken outside the city were considered, we might expect the proportion of profile types B and E to be reduced relative to other types during the late forenoon and early afternoon hours, but this is not the case during the late forenoon, when there is no change. During the early afternoon, the proportion of Type E profiles (there are no Type B profiles during this time period) is about 10.8 percent in the total sample and 6.1 percent among the profiles taken outside the city. The expected effect is present, but not very pronounced.

Even if profiles measured above the city are excluded, this does not appreciably alter the chances of finding a profile with uniform ozone concentrations through the mixing layer. Figure 74 is a scattergram relating mixing-layer ozone concentration to surface concentration

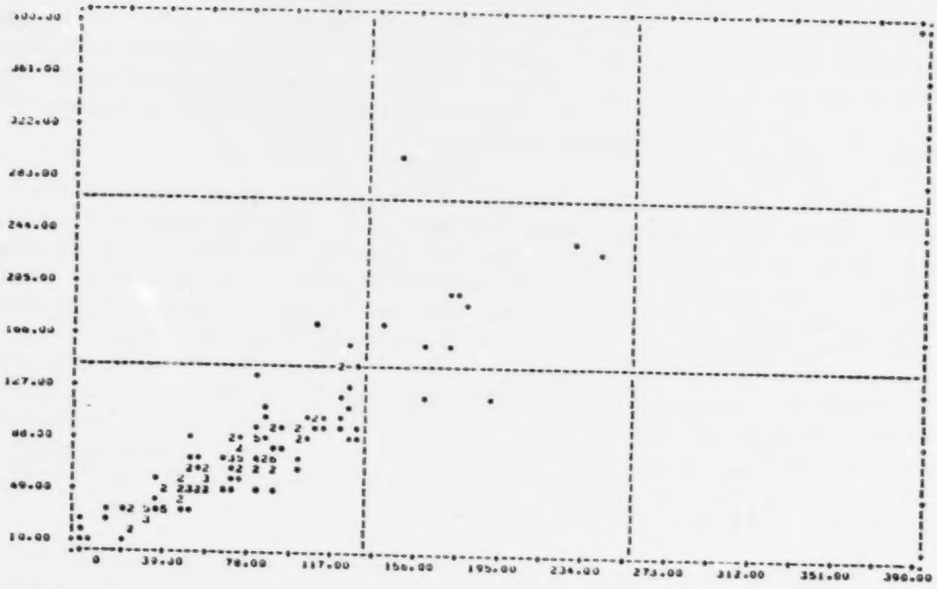


FIGURE 74 SCATTERGRAM OF AVERAGE MIXING-LAYER OZONE CONCENTRATIONS VERSUS SURFACE CONCENTRATION FOR ALL MEASUREMENTS BETWEEN 0900 AND 1500 LST

for all the observations made between 0900 and 1500 LST. Obviously, the relationship is close enough to be quite useful. The regression line shown in the figure estimates average mixing-layer concentrations with a standard error of about 21 ppb.

Probably an astute analyst could use readily available meteorological observations and radiosonde data to select cases with sufficient mixing to ensure that the surface ozone concentration was representative of that throughout the mixing layer. Some attempts were made to select data points from among those shown in Figure 74, on the basis of atmospheric stability class and location relative to the city. When only those profiles measured during periods when the atmosphere was moderately or extremely unstable are included, the standard error of the regression estimate drops from about 21 ppb to about 13 ppb. However, the correlation is not as good, being reduced to 0.87 from 0.91. Furthermore, the relationship between surface and mixing-layer ozone concentrations in the data set for unstable atmospheric conditions is not one of near-equality, as it is in Figure 74. The slope of the line in the unstable data set is only 0.7 (as opposed to 0.96), and the intercept is 21 ppb (as opposed to 7 ppb).

E. Summary of Profile Features for Other Photochemical Pollutants

It should be apparent from the preceding discussions that one of the major factors in the determination of vertical profile shapes for ozone is the destruction process. In general, destruction takes place near the surface by reaction with NO, or with natural, gas-phase destructive agents (Vukovich, 1973), or by contact with the surface itself. Destruction is largely responsible for the formation of profiles of types B, E, and F. If there were no destruction near the surface, the type A profile would not evolve to a type B, and the type D would not evolve to type E. Thus, if a pollutant has no sink near the surface it would be unlikely to find profile shapes like type B or E.

If instead of a sink at the surface, a pollutant has sources there, then one might expect to find a much larger percentage of profile types C and D. If the pollutants emitted at the surface were thoroughly distributed through the mixing layer, then the profile would be of type D. If the mixing were not complete, then the profile would be type C. Most of the major pollutant groups, e.g. NMHC and NO_x are not destroyed at the surface. In general, their sources are near the surface. Unfortunately, only a few reliable profile measurements have been made for these pollutants, so it is not possible to develop a comprehensive statistical description of observed profile types as was done for ozone.

Nephelometer measurements have been made more extensively than those for NMHC and NO_x. Nephelometer measurements give an indication of the concentration of submicron particles in the atmosphere. If it is presumed that the aerosol source and behavior are similar to the pollutants of interest, then the profiles of nephelometer readings can be examined as surrogates for the other pollutants. Even when this is done, the available data are still fewer than for ozone, partly because fewer airborne nephelometer measurements were made, and partly because ground based nephelometer measurements that would allow us to extrapolate the profiles to the ground are not available.

The useable profiles of nephelometer readings from St. Louis, Washington, D.C., and Los Angeles have been examined; 116 profiles were subjectively classified according to shape. None of the profiles fell into either category B or E. This may be because the lowest part of many profiles were not available, but it is probably due to the lack of strong sinks near the surface.

Table 17 summarizes the joint frequencies of occurence of various combinations of ozone and nephelometer profile types. The most obvious thing about the table is that type D profiles are by far the most commonly occurring type. In essence, this shows that pollutants that are emitted near the surface, but that have no appreciable sinks there, tend to be uniformly mixed through the boundary layer. The differences

Table 17

OZONE PROFILE TYPES OBSERVED
WITH VARIOUS NEPHELOMETER PROFILE TYPES

Nephelometer Profile Type	Ozone Profile Type						Total
	A	B	C	D	E	F	
A	6	0	0	0	0	1	7
C	2	0	0	1	0	0	3
D	17	3	6	31	9	23	89
F	1	2	0	1	5	8	17

between the shapes of the ozone profiles and the concurrent nephelometer profiles are generally explainable in terms of the differences between pollutants that have a source at the surface and those that have a sink. For example, when the ozone profile is type A. nearly all the nephelometer profiles were either the same type (A) or type D, indicating that aerosol material had been released into the boundary layer although no ozone had been produced recently within the boundary layer. When the ozone profile was of type B, the nephelometer readings were of type D because aerosol had been added, rather than removed at the surface. In some cases, the type B ozone profiles were accompanied by type F nephelometer profiles, which suggests that there may have been some removal of aerosol near the surface, but not as much as for ozone.

All ozone profiles of type C were accompanied by type D nephelometer profiles. This indicates that in those cases the mixing of aerosol through the boundary layer was more complete than it had been for ozone and its precursors. Nearly all the type D ozone profiles were accompanied by type D nephelometer profiles. In one case, the nephelometer profile was of type C, indicating that the aerosols had not been as completely mixed as the ozone, but this was quite unusual. Similarly, there was only one case where the nephelometer profile was type F when the ozone profiles was type D.

As was noted before, the type E ozone profiles evolve from type D when ozone is destroyed near the surface at a rate faster than it can be mixed downward from aloft. Thus, for those pollutants that are not destroyed near the surface, the profile should remain a type D. Table 17 shows that most of the type E ozone profiles were accompanied by type D nephelometer profiles, as expected. In five instances, the nephelometer profile was of type F which suggests that there may have been some losses within the mixing layer, but not severe enough to produce a type E shape profile. Finally, Table 17 shows that when ozone was found isolated in a layer aloft, in a type F profile, the vast majority of the accompanying nephelometer profiles were of type D. Again, this is a reflection of the lack of strong sinks for the aerosol.

The question remains, do the precursors, NMHC and NO_x, behave in the same way that the nephelometer observations of aerosol concentration behave? Eleven NMHC profiles were available for comparison with nephelometer profiles from the Los Angeles basin. In all cases, the nephelometer profile was of type D. In seven instances, the NMHC profile was the same. Three of the remaining four were type C, indicating that the NMHC had not been mixed as thoroughly in the boundary layer as had the particulates. The one remaining case was type A, as was the ozone profile at the time.

There are sixteen NO_x profiles from the Los Angeles basin that can be compared to nephelometer profiles; fourteen of these nephelometer profiles are of type D. Two of the NO_x profiles associated with type D ozone profiles are type C and one is type A. There is another type D profile of NO_x associated with a type F nephelometer profile. Finally, there was one instance when both the nephelometer and NO_x profiles were of type F.

In summary, the nephelometer profiles seem to behave much like the precursor profiles. Both categories of pollutants most commonly display profiles that are type D, as one would expect of materials with sources rather than sinks at the surface. Type D profiles indicate that the precursors emitted at the surface are rather quickly mixed within the boundary layer and achieve a reasonably uniform concentration profile. Under such conditions, precursor measurements made at the ground should be reasonably representative of concentrations existing aloft. It appears that if conditions are such that the ozone profiles are of type A or type D, then one can reasonably expect surface precursor observations to be representative of conditions through the boundary layer. It should be understood, that the precursors referred to are NMHC and NO_x. The individual oxides of nitrogen, such as NO and NO_2, may be involved in reactions with ozone. In such cases, the processes that reduce ozone concentrations near the surface might also reduce the NO concentration and increase the NO_2 concentrations in the lowest layers.

The above analysis is necessarily tentative and uncertain because of the very few measurements that are available. Physical reasoning suggests that the dust concentrations represented by the nephelometer data should behave in a manner similar to other pollutants that are not formed or removed rapidly. Nevertheless, more data from future field studies will be needed before one can be certain that the nephelometer data do serve the intended role as surrogates for the behavior of oxides of nitrogen and hycrocarbons.

IV VARIATIONS IN THE MIXING LAYER AND WINDS NEAR CITIES

A. Background

The four most important meteorological factors governing ozone concentrations in the vicinity of cities are probably transport by the wind, availability of sunshine, mixing and dilution by turbulent diffusion, and restrictions to the vertical extent of mixing. In general, the transport winds can be inferred from surface wind measurement; pilot balloon observations of winds aloft are also sometimes available; and weather service analyses of conditions at the 850-mb level (approximately 1500 m) are also useful for determining transport, but the city will change the wind during its passage and these changes should be considered. Available sunshine can usually be estimated from conventional cloud cover observations and time of day. Similarly, atmospheric stability can be estimated from surface weather observations (e.g. Turner 1964; Ludwig and Dabberdt, 1976), but the atmosphere will be less stable over the city than over its environs because of differences in surface roughness and heat capacity (see, e.g., Ludwig and Dabberdt, 1976).

While most of the important meteorological factors governing the distribution of chemical pollution can be inferred from the conventional weather observations available throughout the day (often at hourly intervals), the mixing depth is not so easily obtained. Its determination generally requires radiosonde observations, which are made only twice daily and at rather widely spaced locations. Therefore, it is important to have some understanding of how the mixing depth varies in time and space, so that the rather limited radiosonde observations can be usefully interpreted. This section discusses the spatial and temporal changes in the mixing layer and winds.

B. The Mixing Layer

Table 18 shows how mixing depth was distributed during the different time intervals for the data sample considered in this report. For the nighttime hours, the observed mixing depths were always below 1 km. During the day, greater mixing depths were more common. During the night hours, two-thirds of the cases were less than 500 m. Between 0900 and 1200, only one-third of the cases were less than 500 m, and in the afternoon the proportion of mixing depths less than 500 m was less than one-sixth. Correspondingly, the numbers of cases of mixing depths in the 1500- to 2000-m range increased during the day from a small fraction before 0900 to about one-fourth during the afternoon. A chi-square test (Nie et al., 1975) of the data shown in Table 18 indicates that the differences in the frequency distribution from one time of day to another are highly significant; the chance probability is less than 0.01 percent.

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Table 18

MIXING DEPTH AT DIFFERENT TIMES OF DAY

MIXING DEPTH — km	COUNT ROW PCT COL PCT TOT PCT	TIME PERIOD BEFORE 600 1.	600-900 2.	900-1200 3.	1200-1500 4.	1500-1800 5.	1800-2100 6.	2100-2400 7.	ROW TOTAL
LESS THAN .5	1.	2 2.3 50.0 .8	40 46.0 71.4 15.8	26 29.9 35.6 10.3	11 12.6 16.4 4.3	6 6.9 12.2 2.4	0 0 0 0	2 2.3 100.0 .8	87 34.4
.5 TO 1	2.	2 2.8 50.0 .8	11 15.3 19.6 4.3	21 29.2 28.8 8.3	26 36.1 38.8 10.3	12 16.7 24.5 4.7	0 0 0 0	0 0 0 0	72 28.5
1 TO 1.5	3.	0 0 0 0	3 7.0 5.4 1.2	11 25.6 15.1 4.3	11 25.6 16.4 4.3	18 41.9 36.7 7.1	0 0 0 0	0 0 0 0	43 17.0
1.5 TO 2	4.	0 0 0 0	2 4.1 3.6 .8	15 30.6 20.5 5.9	18 36.7 26.9 7.1	13 26.5 26.5 5.1	1 2.0 50.0 .4	0 0 0 0	49 19.4
2 TO 2.5	5.	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0	1 100.0 50.0 .4	0 0 0 0	1 .4
2.5 TO 3	6.	0 0 0 0	0 0 0 0	0 0 0 0	1 100.0 1.5 .4	0 0 0 0	0 0 0 0	0 0 0 0	1 .4
	COLUMN TOTAL	4 1.6	56 22.1	73 28.9	67 26.5	49 19.4	2 .8	2 .8	253 100.0

There is some suggestion in Table 18 that the transitions between the low nighttime mixing depths and the higher daytime values and back again to the low nighttime values may occur over rather short periods of time. Case studies verify this. Auer and Eaton (1976), Endlich et al. (1978) and Uthe et al. (1978) have examined lidar observations taken during the summer in St. Louis, and provide many examples of transition from nighttime to daytime conditions. Figure 75, from the report of Endlich et al. (1978), illustrates a typical case. The figure shows the distribution of backscatter in the vertical, which is a measure of the distribution of aerosol. Figure 75(b) shows the vertical gradients in the backscatter, with the bright areas representing the largest negative gradients. The increasing depth to which the aerosol was mixed later in the day is apparent in the figure. The heavy line in Figure 75(c) marks the climb of the mixing depth during the morning. From about 1000 to 1115 CDT, the depth of the mixing layer rises from about 350 m to about 1400 m, approximately the height to which aerosol from preceding days had been mixed, as is evident in the figure. Figure 76 is another example of the temporal changes in mixing depth over St. Louis. The rises in mixing depths seen in Figures 75 and 76 are rather typical of what has been found in the analyses of St. Louis lidar data.

A major part of the increase from low nighttime mixing depths to the higher daytime values comes over a period of 1 or 2 hours during the late forenoon. The rise then usually continues more slowly until later afternoon or early evening. Around sunset, as seen in Figure 76, there is often a very rapid transition to the nighttime, shallow mixing-layer conditions. The transition to nighttime conditions is almost discontinuous, whereas the increase in mixing depth usually proceeds over a period of a few hours as the ground heats during the morning and the resulting convection pushes farther and farther upward. At night, the ground cools and a stable layer forms very quickly in the lowest layers. This stable layer damps out the convection so that a new, very shallow mixing layer is established within the previously formed mixing layer. Figures 75 and 77 (from Endlich et al., 1978) provide good examples of this. There is evidence throughout Figure 77 that mixing sometime in the past extended above 1800 m, but the more recent afternoon mixing had carried pollutants only to about 1500 to 1600 m. By 2030-2045 CDT, virtually all the pollutants emitted at ground level were confined within a very shallow layer, no more than 300 m deep. The objective analyses of Endlich et al. (1978) shown in Figure 77(c) shift abruptly from the higher mixing layer to the lower one during this period of time.

The diurnal behavior of mixing depth discussed above was measured in the city of St. Louis. Within a city, nighttime mixing tends to be more vigorous and extends to greater heights than it does outside the city, because of the heat generated and stored in urban structures (Tyson et al., 1973). Uthe et al. (1978) operated a mobile lidar system in St. Louis to study differences between mixing heights outside the city and those over the city. The lidar was operated along the traffic

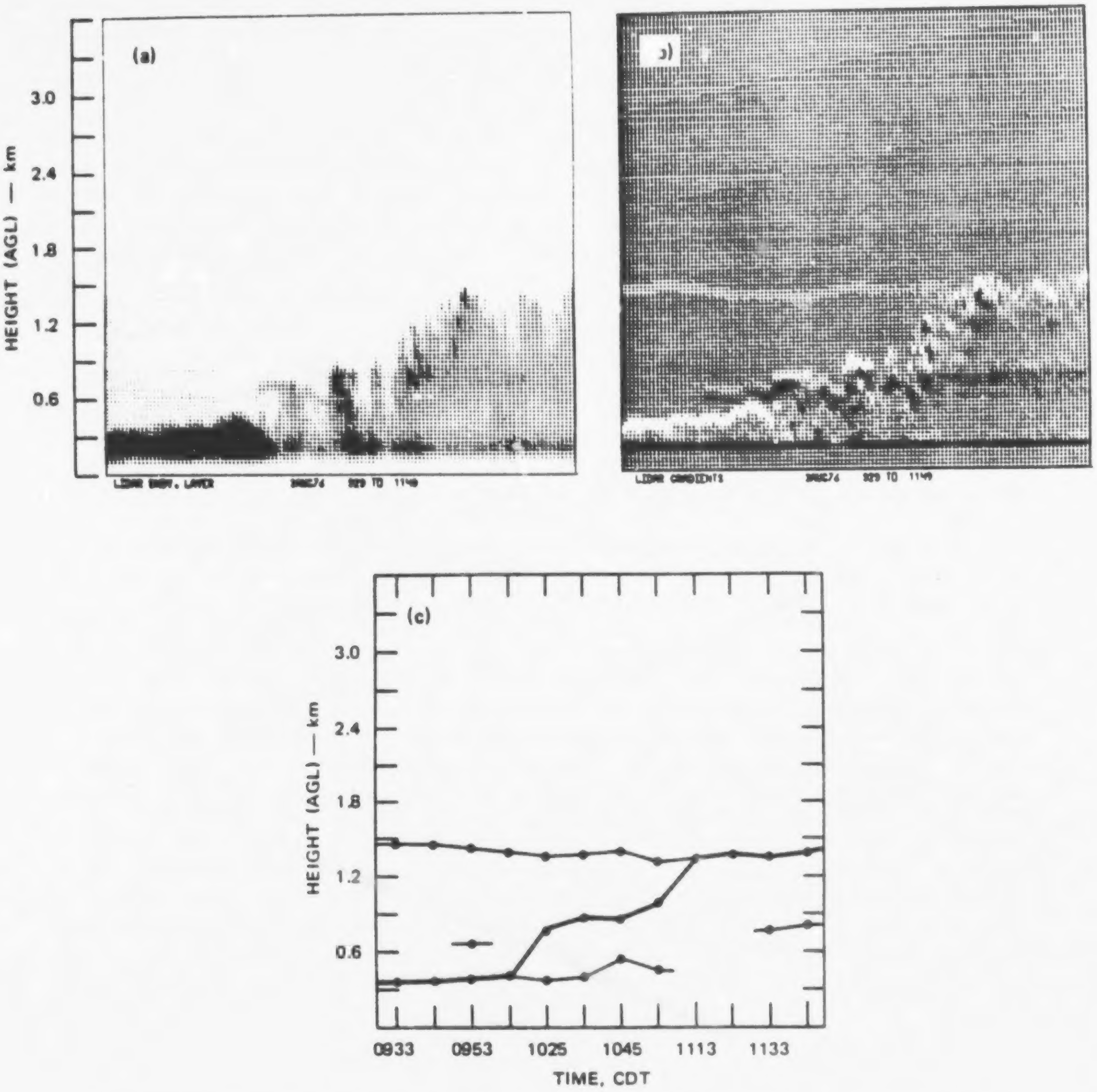


FIGURE 75 GRAY-SCALE DISPLAY OF LIDAR DATA FOR AUGUST 3, 1976 FROM 0929 TO 1145 SHOWING THE CHANGES PRODUCED BY THERMAL MIXING. (a) Backscatter data. (b) Vertical gradients. (c) Objectively identified negative gradients. A heavy line indicates the largest negative gradient, which is the mixing depth.

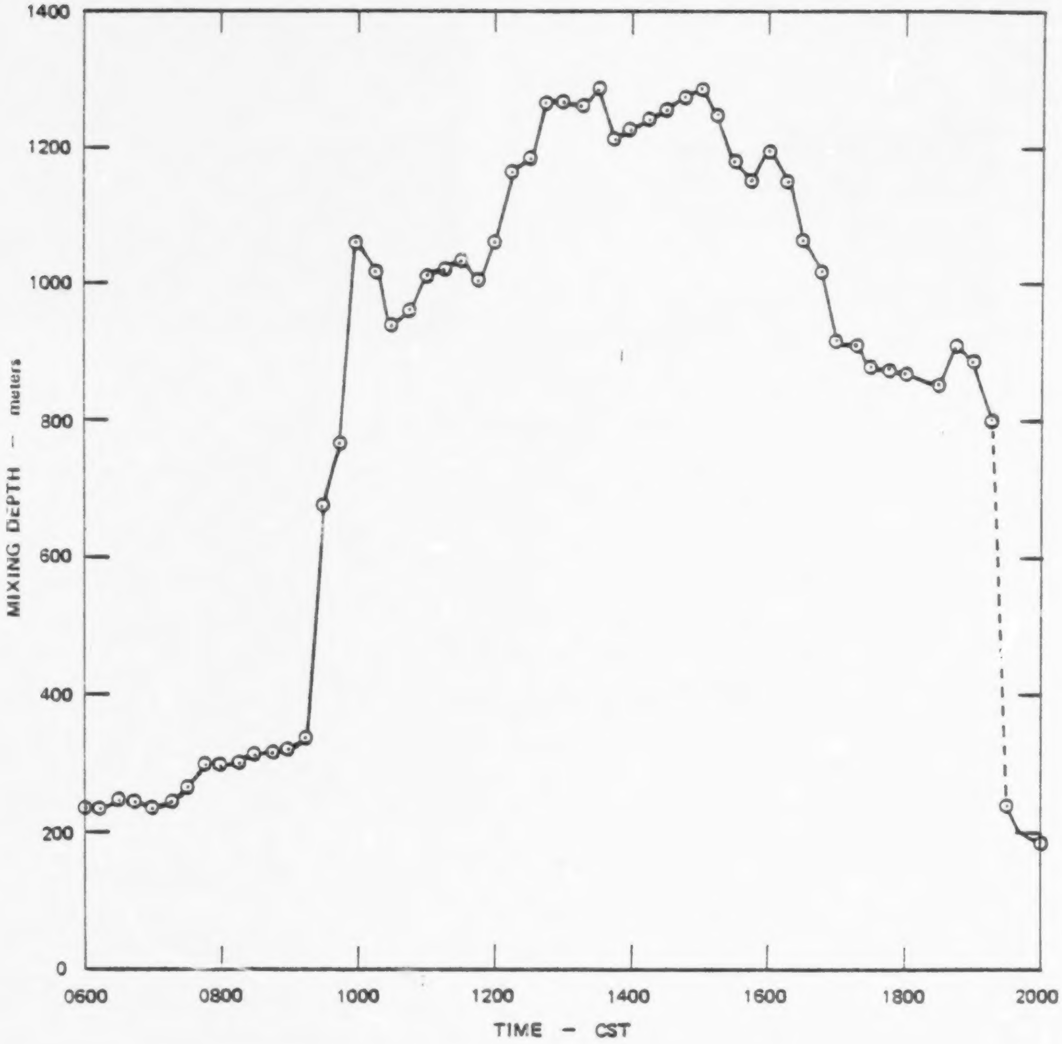


FIGURE 76 DIURNAL CHANGES IN MIXING DEPTH IN ST. LOUIS, AUGUST 9, 1976

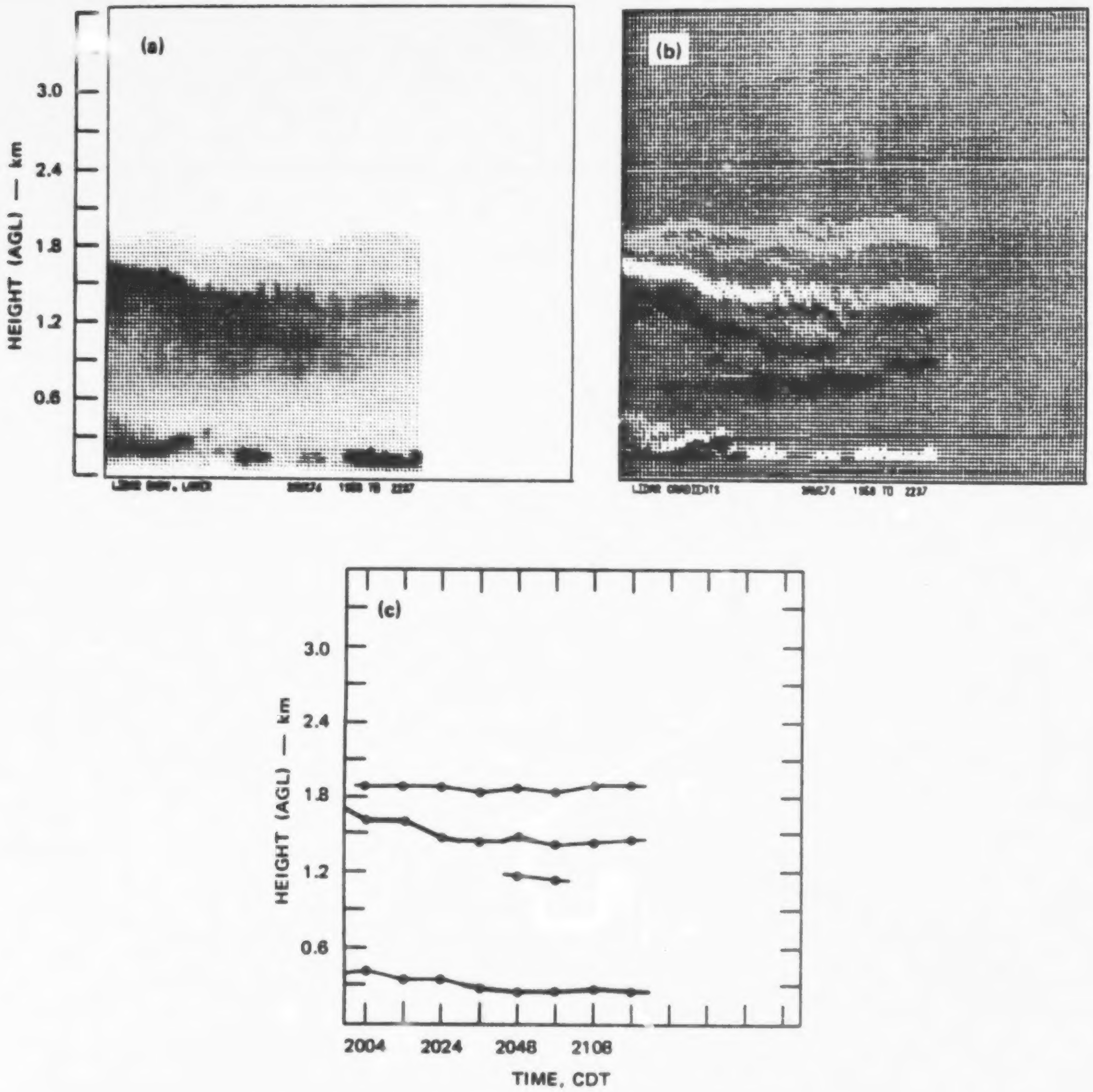


FIGURE 77 GRAY-SCALE DISPLAY OF LIDAR DATA FOR AUGUST 3, 1976 FROM 1958 TO 2124 SHOWING ESTABLISHMENT OF THE MIXING DEPTH AT A LOW LEVEL

(a) Backscatter data. (b) Vertical gradients. (c) Objectively identified negative gradients.

route shown by the heavy line between Site 2 and Site 4 in Figure 78. Auer and Eaton (1976) analyzed the data as contours of mixing depth on a time/distance mapping. Their analysis indicated that the rise in the urban mixing depth precedes the rise in the rural mixing depth by thirty to forty-five minutes. Earlier studies by Uthe and Russell (1973) indicated that the morning rise of the rural mixing depth lagged behind the rise in the city by one to two hours.

Uthe et al. (1978) have used the results of Auer and Eaton (1976) to determine minimum and maximum mixing depths observed along the transect line shown in Figure 78. The minima and maxima were plotted as functions of time for eight different days. The results are shown in Figure 79. The numbers near the data points on the curves are the distance (km) from the Gateway Arch at which the minimum or maximum was observed. Positive values are east of the Arch and negative values are to the west. The Arch is just east of the central business district of St. Louis and near the Mississippi River. The metropolitan area extends east of the Mississippi River to include East St. Louis and other Illinois suburbs.

Inspection of Figure 79 shows that nearly all the maximum mixing depths were in urban areas, within about ten kilometers of the Arch. The minimum mixing depths were, in almost all cases, in the more rural locations well removed from the Arch. The difference between maximum and minimum mixing depth, i.e. between rural and urban mixing depth, tends to increase during the daytime; the greatest differences are observed in the afternoon. The average difference between all maximum (urban) and minimum (rural) mixing depths was computed to be 203 meters. Because Uthe et al. (1978) used the highest and lowest values along the lidar route, the average that they obtained probably overestimates the difference between rural and urban conditions. Figure 80 shows Auer and Eaton's (1976) analysis of the same data, using more typical urban and rural values. Figure 80 shows that the mixing depths over the city are greater than over the rural areas, both during the daytime and at night and that this difference increases with time of day to an average of about 160 or 170 meters. There are some indications that the mixing depths later in the afternoon are more nearly constant than indicated by the figure. An empirical formula exists (Ludwig, 1970) for estimating the depth of the mixing layer over a city, using rural observations of the lapse rate in the lowest layers of the atmosphere. It was derived from an empirical relationship between the magnitude of the urban heat

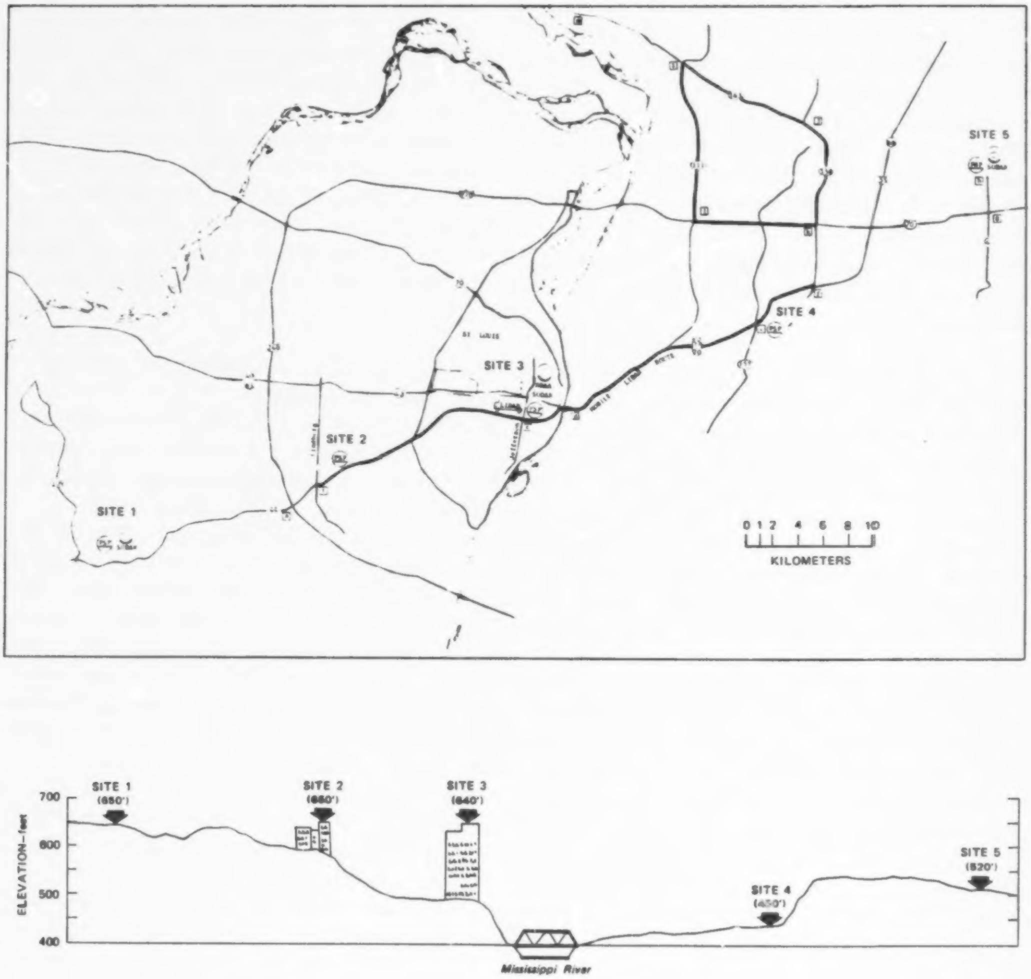


FIGURE 78 LOCATION AND ELEVATION OF THE LIDAR ROUTE USED DURING THE 1975 METROMEX STUDY (Uthe et al., 1978)

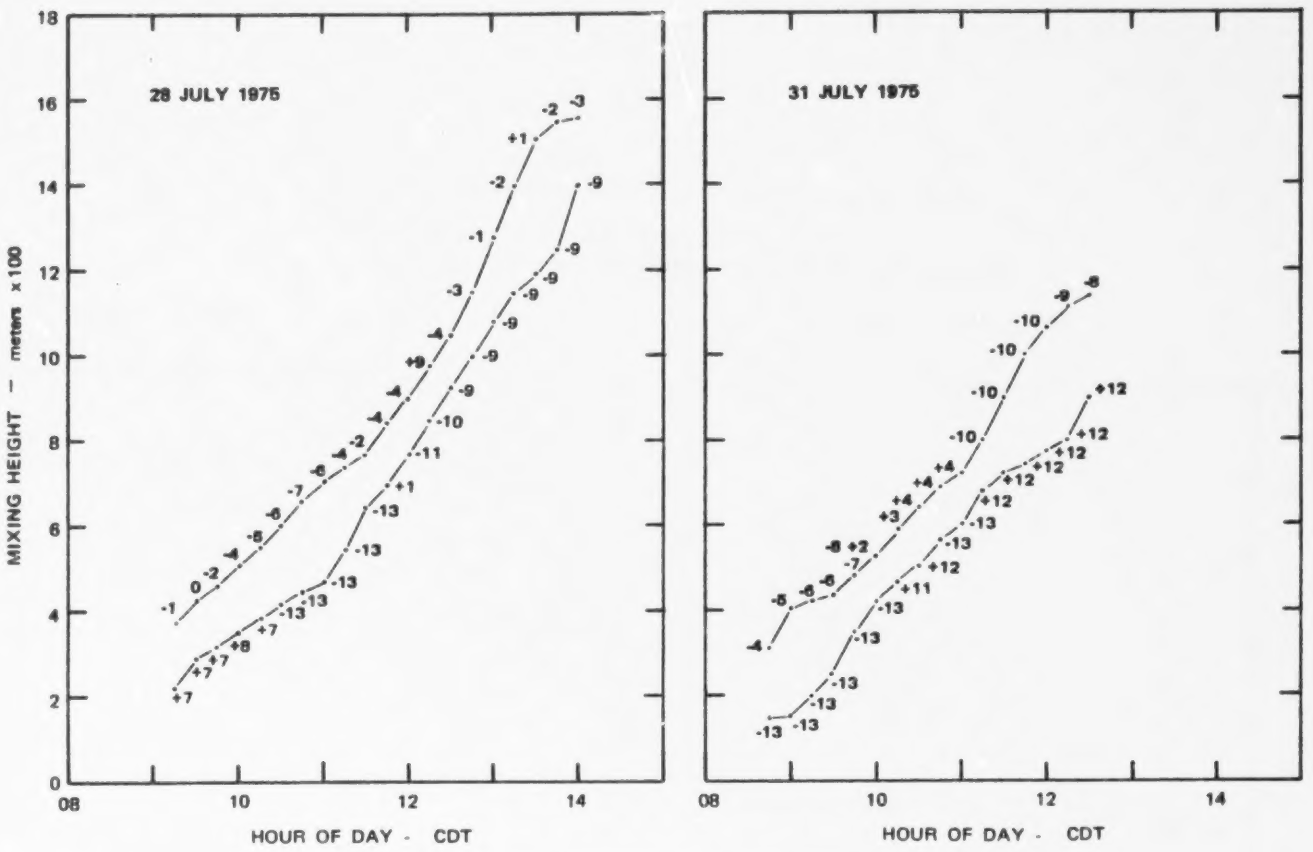


FIGURE 79 LIDAR-OBSERVED MAXIMUM AND MINIMUM MIXING DEPTHS AS A FUNCTION OF TIME (Uthe et al., 1978)

Positive numbers indicate distance (km) east and negative numbers west of the Gateway Arch

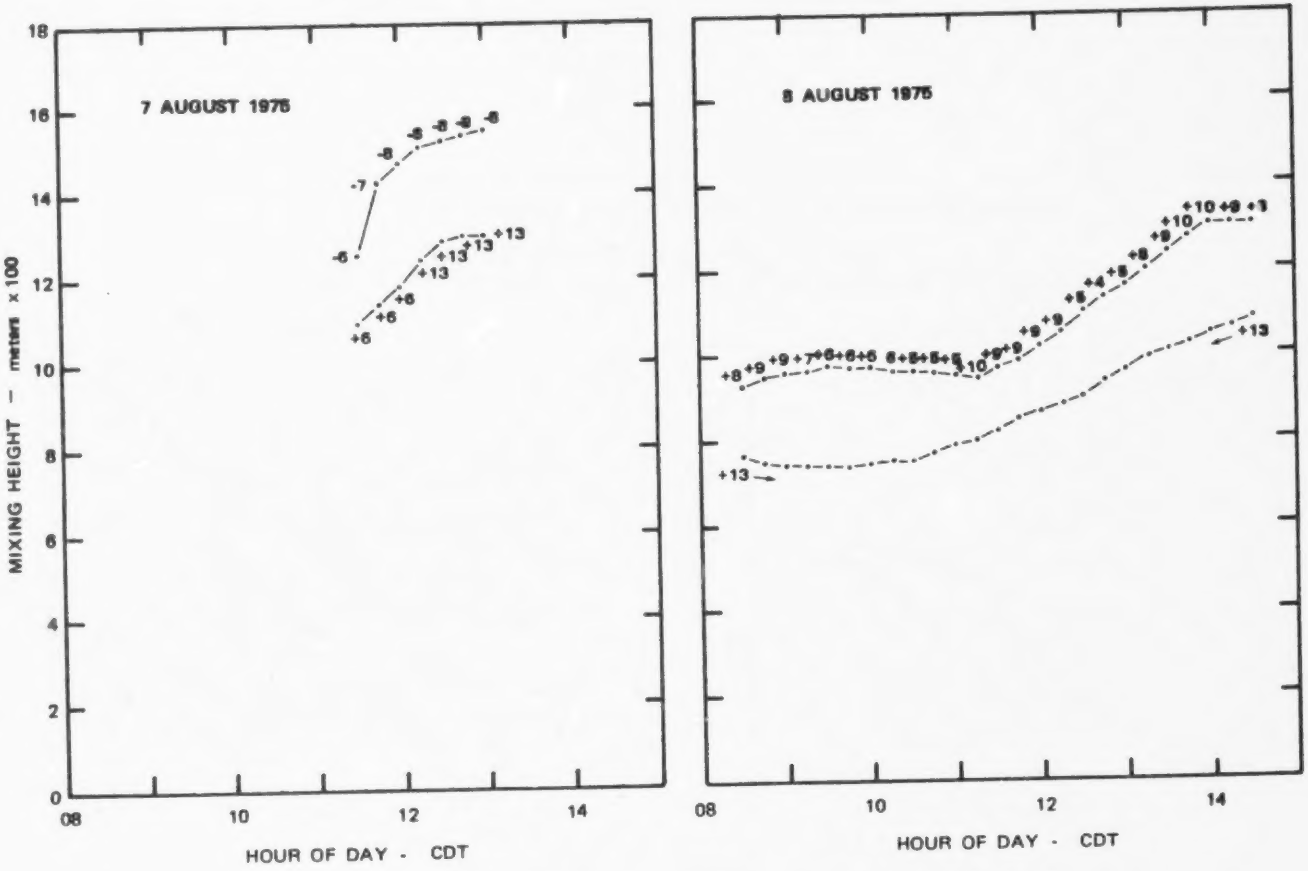


FIGURE 79 LIDAR-OBSERVED MAXIMUM AND MINIMUM MIXING DEPTHS AS A FUNCTION OF TIME (CONTINUED)

Positive numbers indicate distance (km) east and negative numbers west of the Gateway Arch

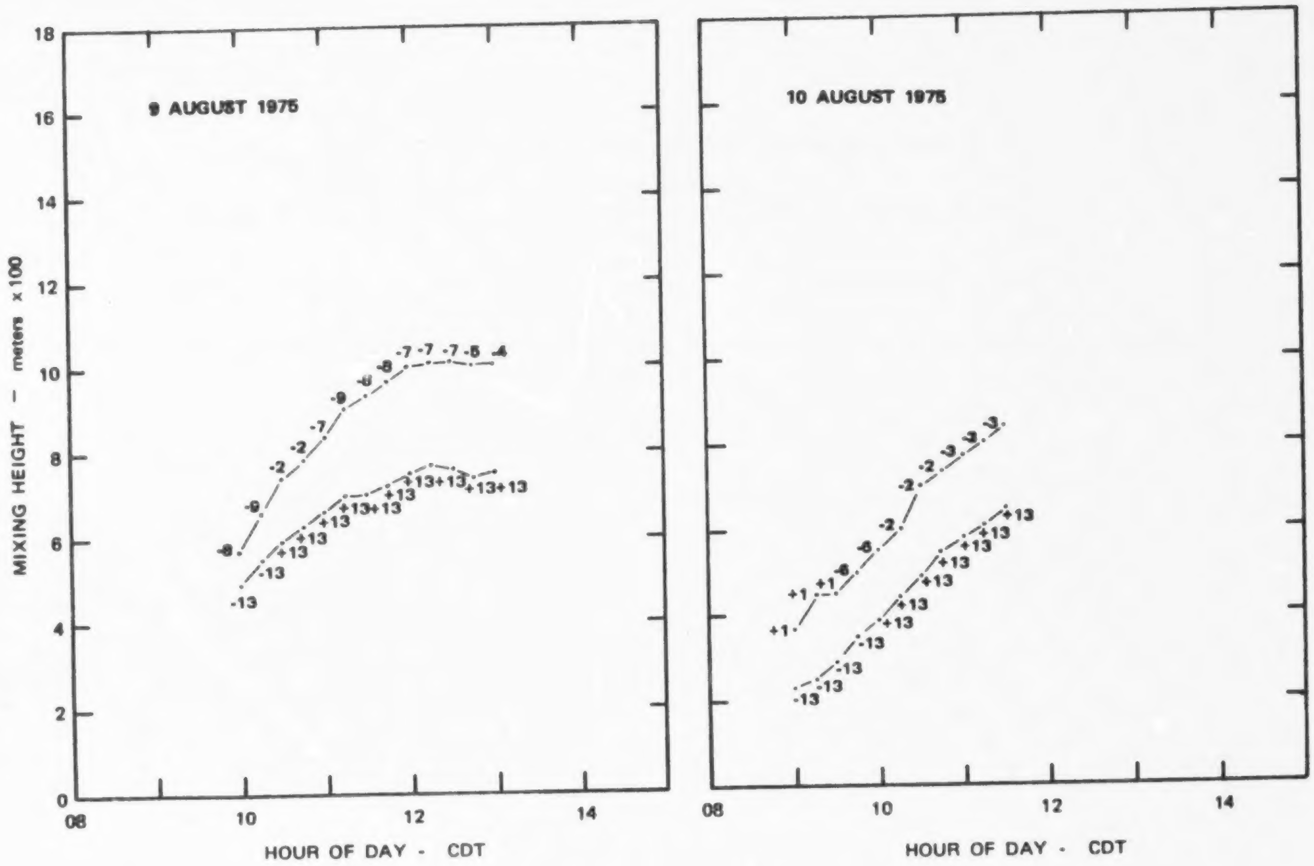


FIGURE 79 LIDAR-OBSERVED MAXIMUM AND MINIMUM MIXING DEPTHS AS A FUNCTION OF TIME (CONTINUED)

Positive numbers indicate distance (km) east and negative numbers west of the Gateway Arch.

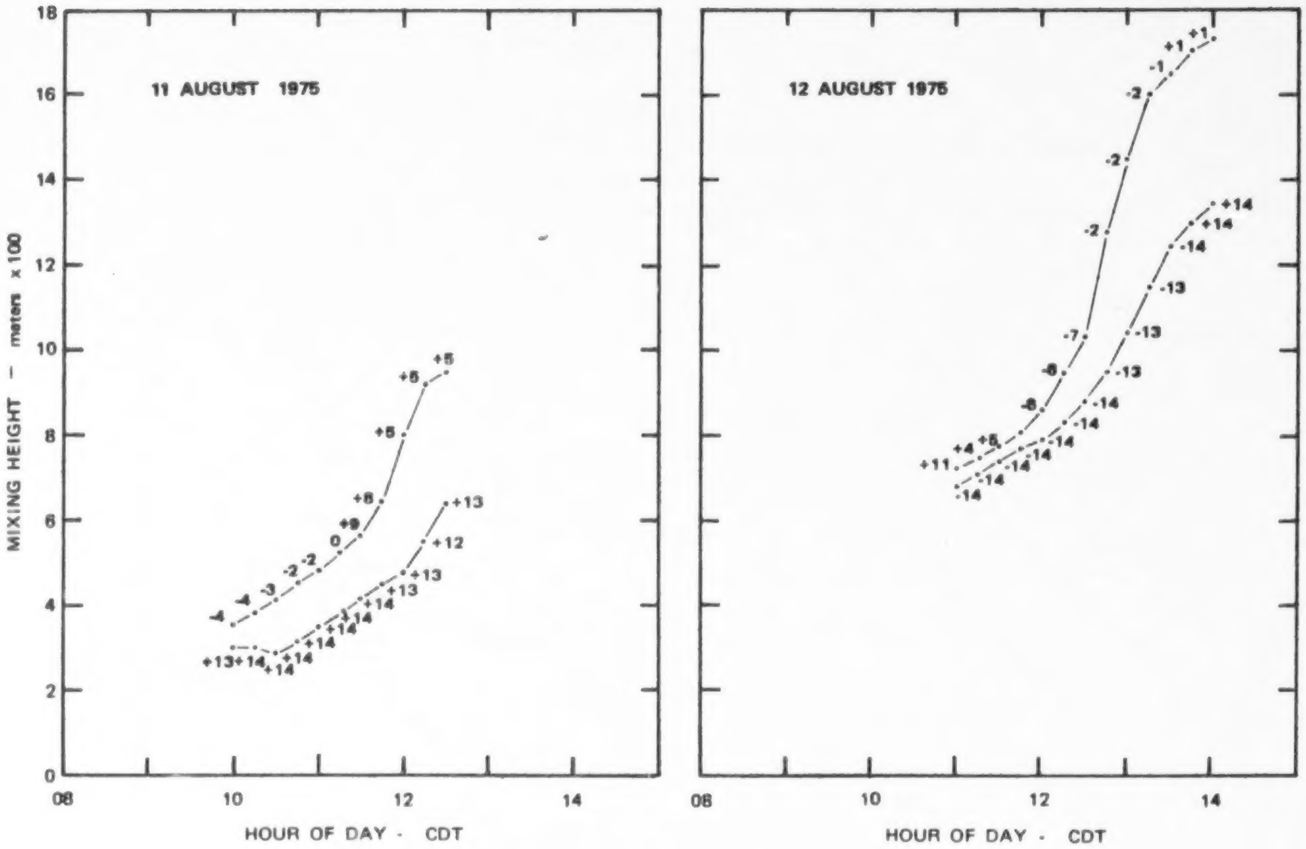
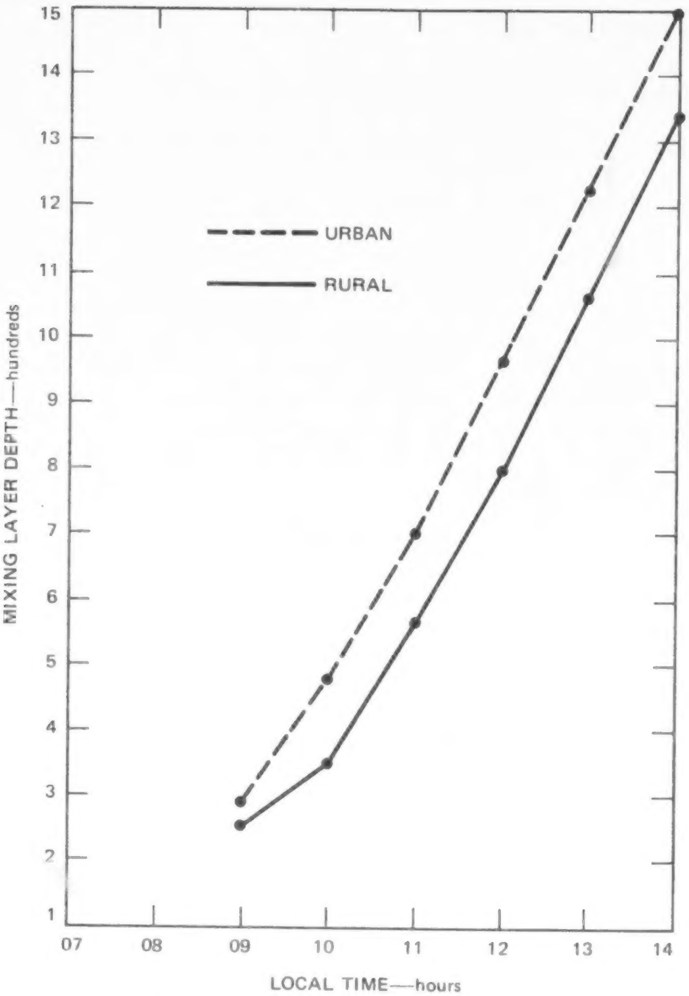


FIGURE 79 LIDAR-OBSERVED MAXIMUM AND MINIMUM MIXING DEPTHS AS A FUNCTION OF TIME (CONCLUDED)

Positive numbers indicate distance (km) east and negative numbers west of the Gateway Arch.



SOURCE: AUER AND EATON, 1976

FIGURE 80 AVERAGE INCREASE IN URBAN AND RURAL INFLUENCES ON THE DEPTH OF THE MIXING LAYER NEAR ST. LOUIS

island and rural lapse rate, using Summers′ (1965) simple heat island model. The relation is

$$h=29.3T\Phi^{0.25}(0.298dT/dp-0.0633)/(pdT/dp-0.287)$$

where

Φ = population of the city

p = average pressure through the depth (in mb)

T = average temperature through the depth (in ^{o}K)

h = depth of the mixing layer over the city (in m)

dT/dp = rate of temperature change with pressure (in ^{o}K/mb), in the lowest layers outside the city

Ludwig and Dabberdt (1973) pointed out an interesting characteristic of the above equation. The equation suggests that there is a minimum positive value that h_{min} can assume, implying a minimum mixing depth for any given city. For typical conditions, e.g. T = 280^{o}K and p = 950 mb, the equation becomes the following, when dT/dP approaches a negatively infinite value:

$$h_{min}=2.6\Phi^{0.25}$$

If one needs to estimate mixing depths in the vicinity of some urban areas, it can be done using the nearest available radiosonde measurements. The mixing depths outside the city can be estimated directly from the temperature and humidity soundings. Holzworth (1967) has described the conventional method for estimating afternoon mixing depth from the afternoon maximum temperature and the morning sounding (in the United States, the morning sounding will typically be the one taken nominally at 1200 GMT). The same sounding can also be used to estimate rural mixing depths at night. Urban mixing depths can be derived from the equation given earlier for nighttime cases and by assuming them to be 100 to 200 m greater than the rural values for daytime cases. The transition from daytime to nighttime conditions can be presumed to take place quite rapidly at around sundown. The transition from nighttime to daytime conditions is more gradual and must be estimated. The curves shown in Figures 75, 76 and 80 will serve as guides, if better information is available.

The preceding discussion applies primarily to simple continental locations. In more complicated locations, especially those involving a water-land interface, the behavior of the mixing depth can be much more complex. Lyons and Cole (1976) describe mixing near the shoreline of Lake Michigan. Edinger (1958) modeled the behavior of mixing in the Los Angeles basin as driven by the diurnal heating cycle and the onshore flow. In these more complicated situations, generalizations of mixing-depth behavior are probably not possible and it will be necessary to examine each such case separately.

C. Winds

Winds are driven by pressure gradients, frictional forces and the Coriolis acceleration. One might expect air flow over the city to be different from that in the environs inasmuch as the pressure gradients around a city are altered by the thermal effects of the city, and the frictional effects of the rough city are different from those of its smoother surroundings.

There is some evidence of thermal effects on urban winds, but the effects are generally weak. At night, when the city is appreciably warmer than its surroundings (i.e., the so-called urban "heat island" effect) warm air rising over the city would be expected to produce a radially inward flow near the surface. Shreffler (1978) has found that there are daytime effects as well; although the daytime heat island intensities are generally less than those at night, the lower daytime stabilities require smaller surface temperature increments to maintain upward motion over the city. In any event, the thermally driven component of the wind is generally limited to about one or two meters per second and tends to be undetectable above the background wind speeds produced by large-scale pressure fields.

Thermal effects also have an indirect effect on wind speeds over cities. The nighttime destabilization of the air over the city results in greater vertical momentum transport, so winds at the lower altitudes will tend to be greater at night in the cities than in their rural surroundings. However, the surface winds are not the only winds of importance to the air quality problem. The integrated wind speeds through the lower layers of the atmosphere will tend to be less over the city throughout the day. At night the stabilization of the lower rural atmosphere isolates the air aloft from surface friction and its slowing effects. In fact, the removal of the friction can result in acceleration as the motions adjust. By contrast, over the city with its greater vertical motions, momentum continues to be lost to the surface.

During the day, the frictional effects are somewhat more direct. An exponential function is frequently used to approximate wind speed changes with height:

$$U=U_o\left\{\frac{z}{z_o}\right\}^{\alpha}$$

where U is the wind speed at height z, while U_o is the speed at some reference height z_o. Munn (1970) reports that Davenport (1968) published the average values for α shown in Table 19 for different types of surface. The table also shows Davenport's (1968) reported averages for

Table 19

VARIATION OF WIND EXPONENT AND THE HEIGHT OF GRADIENT WIND WITH SURFACE CHARACTERISTICS--AFTER DAVENPORT (1968)

Surface Type	Exponent	Altitude of Gradient Wind (m)
Flat, open terrain	0.16	270
Suburban	0.28	390
Build-up urban center	0.40	420

the height of gradient wind, above which the winds become more nearly constant with altitude. Figure 81 (from Singer and Smith, 1970) plots much the same information graphically. There are slight differences in the exponents and the top for the urban profile--Singer and Smith extend it to 500 m before the wind becomes constant versus 420 m for Davenport.

In addition to changes in wind speed with height, there are also apt to be changes in wind direction that are accentuated by the urban roughness. The wind direction near the surface will usually be rotated counterclockwise relative to directions aloft. Munn (1970) reports a case over New York where the change of direction from the surface to the gradient wind level amounts to 59°. According to Munn (1970), the directional shear has been reported by Ariel and Kluichnikova (1960) to vary with atmospheric stability from about 15° with strong instability to 40° during inversion conditions.

One final comment is in order with regard to urban effects on air flow. Over cities, the airflow tends to be more turbulent. Ludwig and Dabberdt (1973) have estimated that a city's effects are about equivalent to one Pasquill-Gifford Stability Class (Pasquill, 1961; Gifford, 1961). Thus, the dispersion of precursor pollutants through the mixing layer will proceed more rapidly over the city than over its surroundings.

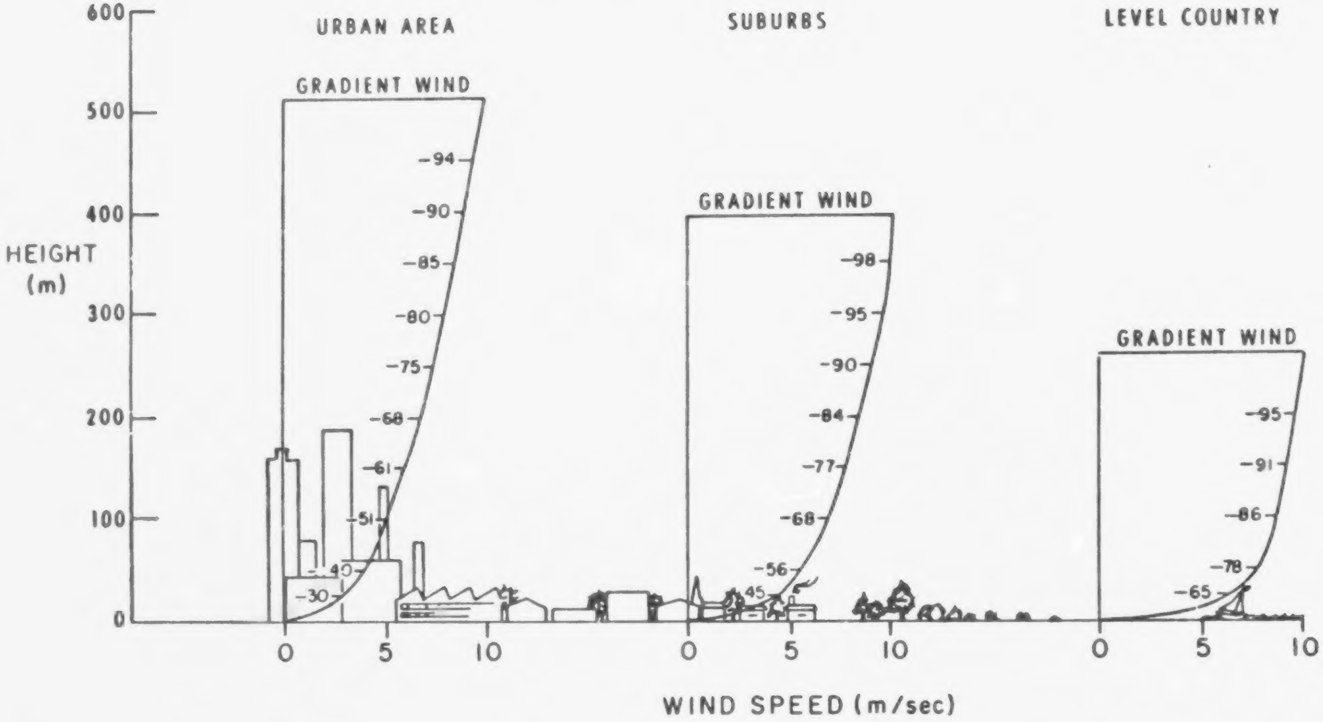


FIGURE 81 TYPICAL WIND PROFILES OVER URBAN, SUBURBS AND RURAL AREAS
(Singer and Smith, 1970)

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